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# JOURNAL OF CHEMICAL EDUCATION

*for November, 1936*

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## *Volume 13, Number 11 Contains*

FRONTISPIECE—EDMUND O. VON LIPPMANN . . . . . 501
EDITOR'S OUTLOOK . . . . . 502
SOME SCIENTIFIC FRIENDS OF SIR WALTER SCOTT . . . . . 503
*Mary Elvira Weeks*
A BIBLIOGRAPHY OF CHEMICAL PLANT DESIGN FOR STUDENTS . . . . . 507
*Helmut M. Haendler and Chester P. Baker*
ON CERTAIN CHEMICAL DEFINITIONS . . . . . 508
*J. K. Senior*
A FURTHER NOTE ON DETERMINATION OF EQUIVALENT WEIGHTS . . . 510
*G. O. Neser*
REACTIVE GROUPS IN ORGANIC REAGENTS AND THEIR APPLICATION IN INORGANIC ANALYSIS . . . . . 511
*Landon A. Sarver*
IMPROVED SODIUM FUSION TECHNIC FOR VOLATILE OR DIFFICULTLY DECOMPOSABLE LIQUIDS . . . . . 515
*A. S. Miceli*
SIMPLER ASPECTS OF ELECTROCHEMISTRY . . . . . 516
*C. W. Bennett*
CRYSTAL CHEMISTRY. III . . . . . 521
*Charles W. Stillwell*
THE TECHNICAL REPORT . . . . . 525
*Alton L. Kibler*
THE TRAINING OF A RUSSIAN CHEMICAL ENGINEER . . . . . 527
*Rudolf Seiden*
PREMEDICAL TRAINING . . . . . 528
*Roy I. Grady and John W. Chittum*
TURNING ACCIDENTS INTO PROFIT THROUGH CAREFUL OBSERVATION . . 530
*Alfred M. Ewing*
NOTES ON THE MOVEMENT OF CRYSTALLINE IODINE IN SILICA GEL . . 532
*Mike A. Miller*
pH DETERMINATIONS IN ELEMENTARY CHEMISTRY . . . . . 534
*Sidney J. French*
EDMUND O. VON LIPPMANN . . . . . 535
*Ralph E. Oesper*
THE CALCULATION OF THE MAXIMUM RESULTS OBTAINABLE BY EXTRACTION WITH IMMISCIBLE SOLVENTS . . . . . 536
*Theodore W. Evans*
A SIMPLE EXPERIMENT IN CHROMIUM PLATING . . . . . 538
*Maxwell Gould*
A CARBON DIOXIDE "GENERATOR" . . . . . 539
*Charles R. Conard*
BIBLIOGRAPHY FOR GENERAL CHEMISTRY FROM SEVERAL PERIODICALS. II . . . . . 540
*Hubert N. Alyea*
ABSTRACTS . . . . . 545
RECENT BOOKS . . . . . 548

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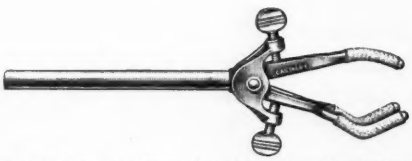

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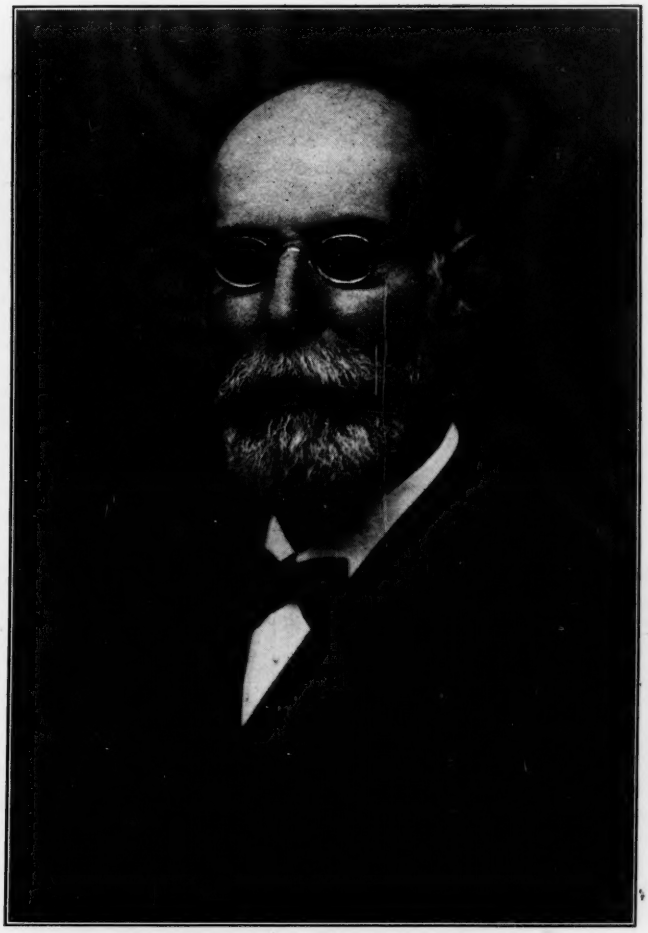

EDMUND O. VON LIPPMANN (1857– )

For biographical note contributed by Dr. Ralph E. Oesper, of the University of Cincinnati, see page 535. Dr. Oesper also lent the photograph here reproduced.

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# EDITOR'S OUTLOOK

PROFESSIONAL RESPONSIBILITY FOR PROFESSIONAL EDUCATION. The increasing activity of the American Chemical Society in matters relating to chemical education, as revealed by the minutes of the Kansas City and Pittsburgh Council meetings,[1] is a development which merits the approval and encouragement of every friend of chemical education and of the Society. Education must be a primary concern of every profession that hopes to maintain and enhance its prestige, and it should be a primary concern of every national professional organization. For the American Chemical Society, as a national association, to ignore educational matters on the ground that it includes within its organization a Division of Chemical Education would be analogous to the oft-deplored practice of carrying one's religion in the name of one's wife.

Aside from the fact that chemical education is very much the business of the Society as a whole, there are certain practical considerations which should not be overlooked. With the extremely limited means at its disposal, the Division of Chemical Education could scarcely undertake any very extensive studies or investigations. Furthermore, with all due respect to the Division membership, and to the coöperative spirit of Society members not carried on the active rolls of the Division, the parent Society enjoys an advantage in the availability of first-class committee personnel. Finally, there can be little doubt that the prestige of the national Society lends greater weight to the findings and recommendations of its committees.

The undertaking of the accrediting of educational institutions offering instruction in chemistry is an instance in point. The task is a thankless one, but it represents a responsibility that the Society has too long sidestepped. The American Medical Association has been far ahead of us in this; even the American Institute of Chemical Engineers has outstripped us.

Unless the accrediting of institutions offering degrees in chemistry degenerates into a polite and meaningless farce it will inevitably be resented and criticized by some members of the faculty and alumni of institutions not approved. It is to be hoped, however, that the accrediting committee will have the courage to set reasonably high standards and to resist all temptations to depart from them. The more reasonable friends of institutions which are excluded from approval will perceive that this very exclusion is a blessing in disguise, for it will constitute the strongest kind of argument in any appeal for funds for the improvement of chemical instruction.

It is encouraging to note that the committee appointed at Kansas City has contented itself with a progress report at Pittsburgh, and that it evidently intends to pursue its task in an orderly and critical manner. We trust that it will have the united and expressed support of the Society membership in this course.

[1] *Ind. Eng. Chem.*, **14**, 145–50 (Apr. 20, 1936); *ibid.*, **14**, 357–9 (Sept. 20, 1936).

*This month's cover picture is a reproduction of a portion of a painting by Elihu Vedder. It has been variously labeled: "The Alchemist" and "The Dying Alchemist." We have been informed, however, that the true title is "The Dead Alchemist." For the photographic copy from which this reproduction was made we are indebted to Dr. Eugene W. Blank.*

# SOME SCIENTIFIC FRIENDS *of* SIR WALTER SCOTT

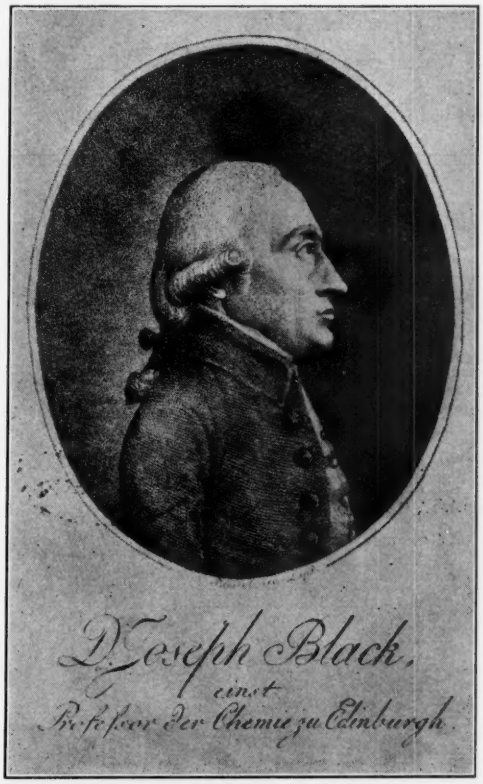
MARY ELVIRA WEEKS

The University of Kansas, Lawrence, Kansas

ALTHOUGH the writings of Sir Walter Scott are not often read by those in search of scientific information, his correspondence and the biography by his son-in-law, J. G. Lockhart, show that the great author of the Waverley Novels was acquainted with Dr. Joseph Black, Dr. William Hyde Wollaston, Sir David and Lady Brewster, Dr. and Mrs. John Davy, and Sir Humphry and Lady Davy. Scott's intimate picture of the characters and home life of his grandfather, Dr. John Rutherford, and of his uncle, Dr. Daniel Rutherford, has been presented in another paper.[1]

Scott's acquaintance with Dr. Joseph Black, the eminent Edinburgh physician and chemist, began in his earliest childhood. Dr. Black had already achieved lasting fame by his masterful elucidation of the chemical changes which take place when limestone is burned and his thorough investigation of the properties of "fixed air," or carbon dioxide.[2] He had also made another important discovery based on an observation of Fahrenheit, mentioned by Dr. Boerhaave, that quiet water may sometimes become much colder than melting snow without freezing, but that, if disturbed, it immediately freezes with sudden rise of several degrees of temperature. One summer day Dr. Black had conceived the idea of investigating this phenomenon quantitatively, but, since no ice was available at that time of year, he had had to wait impatiently until the next December [1761]. By "expending on the ice during its liquefaction, and obtaining from the water during its congelation, as much heat as would have raised the water somewhat more than 140 degrees in its temperature," he had demonstrated the existence of a latent heat of fusion.[3]

At the time of Scott's birth [1771], Dr. Black was the professor of chemistry at the University of Edinburgh and "a favourite physician of that large and active city." In his autobiography Scott wrote:




JOSEPH BLACK, 1728–1799
Professor of Chemistry at the University of Edinburgh.

"I was an uncommonly healthy child, but had nearly died in consequence of my first nurse being ill of a consumption, a circumstance which she chose to conceal, though to do so was murder to both herself and me. She went privately to consult Dr. Black, the celebrated professor of chemistry, who put my father on his guard. The woman was dismissed, and I was consigned to a healthy peasant, who is still alive to boast of her *laddie* being what she calls a *grand gentleman*....."[4]

While Sir Walter Scott was still an infant, his uncle, Daniel Rutherford, was pursuing medical and chemical studies under Dr. Black which were soon to culminate in the publication of his famous thesis in which a clear distinction was made between "mephitic air and nox-

[1] WEEKS, M. E., "Daniel Rutherford and the discovery of nitrogen," J. CHEM. EDUC., **11**, 101–7 (Feb., 1934); *Rev. Scientifique*, **72**, 441–9 (July, 1934).

[2] RAMSAY, SIR W., "The life and letters of Joseph Black, M.D.," Constable and Co., London, **1918**, pp. 20–30, 93–8; DOBBIN, L., "Joseph Black's inaugural dissertation. Crum Brown's translation," J. CHEM. EDUC., **12**, 225–8 (May, 1935); *ibid.*, **12**, 268–73 (June, 1935).

[3] BLACK, JOSEPH, "Lectures on the elements of chemistry," Wm. Creech, Edinburgh, **1803**, Vol. 1, pp. v–lxvi; Preface by John Robison. CRANSTON, J. A., "Bicentenary address on Joseph Black," *Proc. Roy. Phil. Soc.* (Glasgow), **57**, 70–84 (1928–29).

[4] LOCKHART, J. G., "Memoirs of the life of Sir Walter Scott," Adam and Charles Black, Edinburgh, **1862**, Vol. 1, pp. 19–21, 60; Vol. 2, p. 275; Vol. 3, pp. 272, 401–3; Vol. 6, pp. 12, 236–40, 243–6; Vol. 8, pp. 237–8; Vol. 10, pp. 125–6, 131–45.



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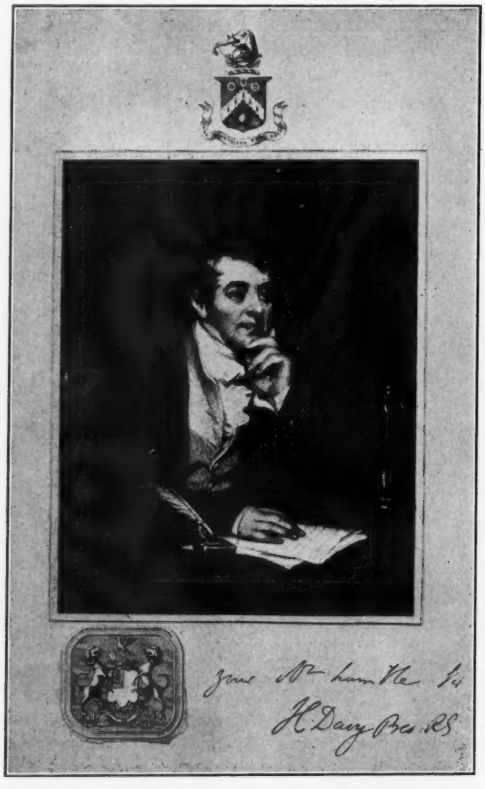
ious air" (carbon dioxide and nitrogen).[5,6] Scott once said of him:

"My uncle was a man of distinguishd talents both as a chemist and botanist & contributed by several of his researches to enlarge the bounds of science by new discoveries. He had also great reputation as a medical man but repeated and prolongd fits of the gout interfered with his profession undermined his health and the expence of keeping a carriage which his infirmities renderd indispensible & that of a decent stile of living consumed his income..... I may add my uncle was of Edgerstanes family & every inch a high-minded and well-born gentleman which partly tended to keep him a poor man as there are modes of pushing ones way in that profession which he could not prevail on himself to practice....."[7]

Sir Walter was twenty-eight years old at the time of Dr. Black's serene and peaceful death, and had already published some original poems and translations.



SIR HUMPHRY DAVY, 1778–1829
Professor of Chemistry at the Royal Institution, London.

When Scott first met Humphry Davy at Wordsworth's home in 1804, the young chemist was at the beginning of his brilliant career. His paper on the uses of astringent vegetables in tanning had appeared in the *Philosophical Transactions* in the preceding year. Scott was delighted with "... the simple and unaffected style of Davy's bearing—the most agreeable characteristic of high genius."[4]

In the following year Scott and Wordsworth were accompanied on one of their short excursions to the Lakes of Cumberland and Westmoreland "... by an illustrious philosopher who was also a true poet—and might have been one of the greatest of poets had he chosen."[4] Lockhart once heard Wordsworth say that "... it would be difficult to express the feelings with which he, who so often had climbed Helvellyn alone, found himself standing on its summit with two such men as Scott and Davy."[4]

The friendship and mutual admiration deepened, and, after Davy's marriage to Sir Walter's distant cousin (Mrs. Apreece, "... lioness of the first magnitude in Edinburgh"), the relationship became more intimate.[4] On July 16, 1812, Scott wrote to Lord Byron, "the fair, or shall I say the sage, Apreece that was, Lady Davy that is, is soon to show us how much science she leads captive in Sir Humphrey [*sic*]. . ."[4] The wealthy bride and her recently knighted husband were among the first guests to enjoy Scott's hospitality at Abbotsford.[4]

Davy had now reached the zenith of his fame. The masterful decomposition of the fixed alkalies and alkaline earths, the preparation and exhibition of the new flammable metals, the elucidation of the chemical changes produced by the voltaic current, and the isolation of boron had made his name known and honored throughout the scientific world, and his lectures at the Royal Institution were being frequented not only by chemists and physicists but by ladies and gentlemen of fashion and by persons distinguished in literature and the arts. When the poet Coleridge was asked to give his reason for attending them so regularly, he replied, "... in order to increase my stock of metaphors."[8]

When Scott's prosperity was at its height, he entertained in princely fashion, and Lockhart's lively description of one of the famous hunting parties in 1820 presents Sir Humphry Davy and Dr. William Hyde Wollaston in a most pleasing light:

"Sir Walter, mounted on Sibyl, was marshalling the order of procession with a huge hunting-whip; and among a dozen frolicsome youths and maidens ..... appeared, each on horseback, each as eager as the youngest sportsman in the troop, Sir Humphry Davy and ..... Dr. Wollaston..... But the most picturesque figure was the illustrious inventor of the safety-lamp." [Since Davy had come prepared for angling rather than for hunting, he was wearing] "..... a brown hat with flexible brims, surrounded with line upon line, and innumerable fly-hooks —jack-boots worthy of a Dutch smuggler, and a fustian surtout dabbled with the blood of salmon." [Lockhart added that] "..... Dr. Wollaston was in black, and with his noble serene dignity of countenance, might have passed for a sporting archbishop....."[4]

Dr. Wollaston had already discovered palladium and rhodium and had devised a process for rendering platinum malleable which had made possible the widespread

[5] MCKIE, D., "Daniel Rutherford and the discovery of nitrogen," *Sci. Progr.*, **29**, 650–60 (Apr., 1935).
[6] DOBBIN, L., "Daniel Rutherford's inaugural dissertation. Crum Brown's translation," J. CHEM. EDUC., **12**, 370–5 (Aug., 1935).
[7] GRIERSON, H. J. C., "The letters of Sir Walter Scott," Constable and Co., London, **1934**, Vol. 6, pp. 82–4.
[8] PARIS, "The life of Sir Humphry Davy," Colburn and Bentley, London, **1831**, Vol. 1, p. 138; Vol. 2, pp. 459–63.

use of that metal. His scale of chemical equivalents had been published in December, 1813, and he had served for twelve years as secretary of the Royal Society. Although he lacked Davy's eloquence and enthusiasm, Dr. Wollaston had remarkable skill in devising experiments and great precision of observation, thought, and speech.[9]

As a guest of Henry Cavendish he often attended the weekly dinners of the Royal Society, and he was, in fact, almost the only person to be honored by the friendship of that great scientific recluse. Wollaston used to take pleasure trips to Scotland and Ireland, sometimes with Smithson Tennant, the discoverer of osmium and iridium, and sometimes with Davy. Occasionally he went on horseback to the home of Sir John Sebright, where he met many persons of distinction, including Berzelius, Sir Walter Scott, and the Irish novelist, Maria Edgeworth, to whom he bequeathed a rhodium pen.[10,11]

The fisherman chemist evidently made an indelible impression on Lockhart's mind, for he wrote:

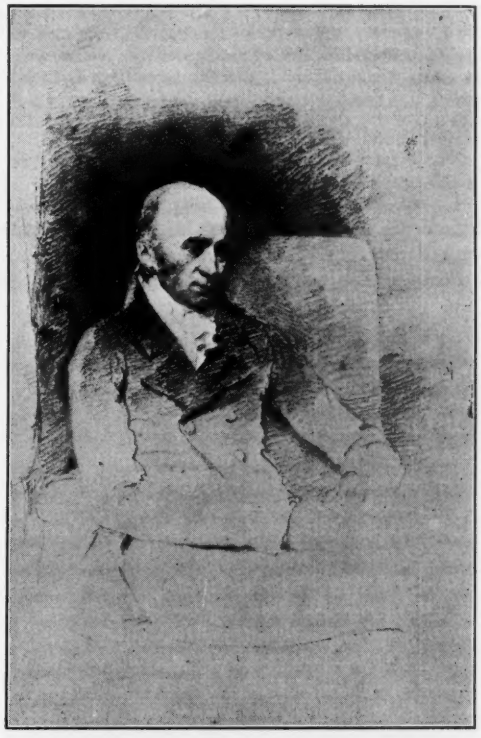
"Davy, next to whom I chanced to be riding, laid his whip about the fern like an experienced hand, but cracked many a joke, too, upon his own jack-boots, and surveying the long eager battalion of bush-rangers, exclaimed—'Good Heavens, is it thus that I visit the scenery of the Lay of the Last Minstrel?' "[4,12]

The mutual admiration between Scott and Davy was so deep, modest, and sincere that Lockhart was led to remark:

"I have seen Sir Humphry in many places, and in company of many different descriptions; but never to such advantage as at Abbotsford..... Davy was by nature a poet—and Scott, though anything but a philosopher in the modern sense of that term, might, I think it very likely, have pursued the study of physical science with zeal and success, had he happened to fall in with such an instructor as Sir Humphry would have been to him, in his early life. Each strove to make the other talk—and they did so in turn more charmingly than I ever heard either on any other occasion whatsoever. Scott in his romantic narratives touched a deeper chord of feeling than usual, when he had such a listener as Davy; and Davy, when induced to open his views upon any question of scientific interest in Scott's presence, did so with ..... clear energetic eloquence, and with a flow of imagery and illustration....."[4]

Although Scott's humblest friends were always welcomed at Abbotsford as cordially as the most celebrated personages from afar, the offer of the baronetcy was most pleasing to his family pride. In a letter to J. B. S. Morritt, written on December 7, 1818, he wrote:

"I hope Sir Walter Scott will not sound worse than Sir Humphry Davy, though my merits are as much under his, in point of utility, as can well be imagined. But a name is something, and mine is the better of the two."[4]



WILLIAM HYDE WOLLASTON, 1766–1828
Secretary of the Royal Society of London.

In later life Scott suffered heavy financial losses, and in reply to a sympathetic letter from Lady Davy he wrote on February 6, 1826,

"..... I beg my kindest compliments to Sir Humphrey [*sic*]; and tell him *Ill Luck*, that direful chemist, never put into his crucible a more indissoluble piece of stuff than your affectionate cousin and sincere well-wisher, Walter Scott."[4]

In 1828, the year before Sir Humphry's death, Scott wrote for the *Quarterly Review* a beautiful appreciation of Davy's book, "Salmonia, or Days of Fly-fishing."[13] In his will Sir Humphry stipulated that Lady Davy was to use and enjoy during her lifetime the different services of plate which the Emperor of Russia and the various coal committees had given him in honor of the invention of the safety-lamp. He also desired that, after her death, if Dr. John Davy should not be in a condition to use the plate, it should be melted and given to the Royal Society to found a gold medal to be awarded each year for the most important discovery in chemistry made anywhere in Europe or Anglo-America.[8] The Davy Medal was therefore founded in 1869 under the will of John Davy.

In his journal Scott mentioned many happy visits with the family of his distinguished neighbor, Sir David Brewster. In a letter written in October, 1824, he said,

[9] "Sir Humphry Davy and Dr. Wollaston," *Phil. Mag.*, [2], **7**, 228–9 (Mar., 1830).

[10] WAYLING, "A short biography of William Hyde Wollaston," *Sci. Progr.*, **22**, 81–94 (July, 1927).

[11] "Aus Berzelius's Tagebuch während seines Aufenthaltes in London im Sommer 1812," translated into German by EMILIE WÖHLER, *Z. angew. Chem.*, **18**, 1946–8 (Dec., 1905) and **19**, 187–90 (Feb., 1906).

[12] DOUGLAS, DAVID, "Familiar letters of Sir Walter Scott," Houghton Mifflin Co., Boston, **1894**, Vol. 2, pp. 216 and 300.

[13] SCOTT, "Salmonia, or days of fly-fishing by Sir Humphry Davy," *Quarterly Rev.*, **38**, 503–35 (July-Oct., 1828).

"My dear Miss Edgeworth: Your philosophical friends or friend's friends [Mr. Marcet* and Mr. Prévost from Geneva] arrived safe at Abbotsford, and of course were received as we would receive every friend of yours. As the Gods have not made me philosophical, I was happy to invoke the assistance of my neighbor, Dr. Brewster, an excellent fellow who talked geology, and mineralogy, and all other *ologies* with them to their hearts' content....."[12]

Sir David Brewster (1781–1868) was already famous for his contributions to optics, and the ever-changing colors and patterns of his kaleidoscope were affording pleasure to adults and children throughout the world.

SIR DAVID BREWSTER, 1781–1868
Scottish physicist and editor. Principal of the University of Edinburgh.

The stereoscope, which he improved in 1849–50, also found a place in most homes of his generation. Since Brewster's researches, like those of Fresnel in France, led to great improvements in the construction of lighthouses, one of the Principals of the University of Edinburgh remarked, "Every lighthouse that burns round the shores of the British Empire is a shining witness to the usefulness of Brewster's life."[14]

He is probably best known to chemists through his researches on polarized light and his discovery that the refractive index of a substance is the tangent of its polarizing angle. He excelled in assembling innumerable facts, and patiently collected data for tables of refractive indices, dispersive powers, and polarizing angles of reflecting substances.[15,16]

In 1831 Scott visited Graham's Island, a submarine volcano which had suddenly appeared in the Mediterranean Sea only to disappear again four months later. Although the island was then near the end of its brief existence and was already beginning to crumble under foot, Scott insisted upon landing. Dr. John Davy, Sir Humphry's brother, prepared a scientific report of the phenomenon for the Royal Society,[17] and Scott wrote a vivid description of the island in a letter to one of his friends.[4] Dr. and Mrs. Davy were at Malta when Scott arrived there, and Mrs. Davy wrote in her diary an amusing account of her quarantine visit to Sir Walter's family, who were standing behind bars at the distance required by law.[4]

John Davy was born at Penzance on May 24, 1790, and was the youngest of five children, of whom Sir Humphry was the eldest. At eighteen years of age he became Sir Humphry's assistant at the Royal Institution, where he admiringly contributed to his brother's success. When he received his medical degree from the University of Edinburgh in 1814, John Davy was made a Fellow of the Royal Society of London, and for the rest of his life he served in various parts of the world as a medical officer.

His first contributions to *Nicholson's Journal*, in which he defended his brother's views regarding the elementary nature of sodium, potassium, and chlorine, were published in 1811.[18] The difficulty encountered by Dr. Davy may be surmised from a comment which Berzelius made in a letter to Dr. Alexander Marcet: "[Gay-Lussac] complains of John Davy, who does not wish to recognize the existence of chloric acid. What would he say of me who recognize neither hydrochloric acid, chlorine, nor the entire bizarre theory?"[19]

In 1812 Dr. Davy allowed a mixture of equal volumes of dry "carbonic oxide gas" (carbon monoxide) and chlorine to enter an exhausted glass receiver, and exposed it to bright sunlight. After about half an hour he noticed that the color of the chlorine had dis-

* Dr. Alexander Marcet had died in 1822.

[12] "Sketch of Sir David Brewster," *Popular Sci. Mo.*, **26**, 546–52 (Feb., 1885).

[15] STEPHEN, LESLIE, "Dictionary of national biography," Macmillan Co., New York City, **1888**, Vol. 6, pp. 299–303; Vol. 14, pp. 195–6. Articles on Brewster and John Davy by ROBERT HUNT.

[16] J. H. G., "Obituary notice of Sir David Brewster," *Proc. Roy. Soc.* (London), **17**, lxix–lxxiv (1869).

[17] DAVY, JOHN, "Notice of the remains of the recent volcano in the Mediterranean," *Phil. Mag.*, [3], **3**, 148 (Aug., 1833); *Phil. Trans.*, **124**, 552 (May, 1834).

[18] DAVY, J., "An answer to Mr. Murray's observations on the nature of potassium and sodium," *Nicholson's J.*, [2], **29**, 35–7 (May, 1811); "On the nature of oximuriatic [*sic*] gas, in reply to Mr. Murray," *ibid.*, [2], **29**, 39–44 (May, 1811); DOBBIN, L., "Chlorine: a phase in its history," *Chemist and Druggist*, **117**, 808–9 (Dec. 31, 1932).

[19] SÖDERBAUM, "Jac Berzelius Bref," Almqvist and Wiksells, Upsala, **1912–1914**, Vol. 1, part 3, p. 131. Letter of Berzelius to Marcet, Dec. 8, 1815.

appeared and that the two gases had combined and become condensed to half their original volume.[20] Since the new gas had been produced by the action of light and since "as yet no other mode of producing it has been discovered," he named it *phosgene*. The photochemical method of preparing it, however, has been superseded by a process involving the use of a charcoal catalyst. Although Gay-Lussac had announced his law of combination of gases by volume only a few years before, Dr. Davy fully appreciated the importance of careful volume measurements and stated at the close of his original paper on phosgene: "This relation of proportions is one of the most beautiful parts of chemical philosophy, and that which promises fairest, when prosecuted, of raising chemistry to the state and certainty of a mathematical science."[20]

Sir Humphry's declaration that the gas formerly regarded as a compound of "muriatic acid" and oxygen is an element, which he named *chlorine*, aroused new interest in its compounds with the metals. In 1812 Dr. John Davy published an extensive research on the properties and composition of the compounds now known as chlorides. He, however, adopted his brother's nomenclature, in which the suffixes *ane* and *anea*, respectively, designated the lower and higher chlorides. Thus, he used the terms *cuprane* and *cupranea* for cuprous and cupric chlorides, *ferrane* and *ferranea* for ferrous and ferric chlorides, etc.[21]

In the same year Dr. Davy also investigated various compounds of "fluoric acid" (hydrofluoric acid), and his experiments were continued by Sir Humphry, who concluded that "fluoric acid" consists of hydrogen and "an unknown supporter of combustion," which he named *fluorine*.[22]

Dr. Davy also published many papers on geological, biological, and medical subjects. His last scientific contribution, "On the temperature of the common fowl," was read to the Royal Society of Edinburgh in 1868, shortly before his death. During most of the fifty-seven years of his scientific career he was in actual medical service in the army. While serving as Inspector-general at Barbadoes he delivered a course of lectures on chemistry, and, since he had edited his brother's treatise on agricultural chemistry, he was able to understand and discuss the agricultural needs of the island.[15] He honored Sir Humphry's memory by editing his works and writing his biography with skill and devotion. Although he lacked Sir Humphry's imaginative gifts, ". . . his sympathy with the cause of his brother's reputation. . . elevated his whole nature and spread through and over his long series of labours the warm light of a sunny memory."[23]

That Scott appreciated the social contacts with his scientific friends is evident from a modest statement in his autobiography:

> "If ..... it should ever fall to the lot of youth to peruse these pages—let such a reader remember that it is with the deepest regret that I recollect in my manhood the opportunities of learning which I neglected in my youth; that through every part of my literary career I have felt pinched and hampered by my own ignorance; and that I would at this moment give half the reputation I have had the good fortune to acquire, if by doing so I could rest the remaining part upon a sound foundation of learning and science."[4]

[20] DAVY, J., "On a gaseous compound of carbonic oxide and chlorine," *Ann. Phil.*, [1], **1**, 56–7 (Jan., 1813); *Phil. Trans.*, **102**, 144–51 (1812); *Nicholson's J.*, [2], **32**, 241–7 (Aug., 1812).

[21] DAVY, J., "An account of some experiments on the combinations of different metals and chlorine," *Nicholson's J.*, [2], **33**, 10–21 (Sept., 1812); *ibid.*, 120–35 (Oct., 1812); *Phil. Trans.*, **102**, 169–204 (1812).

[22] DAVY, J., "An account of some experiments on different combinations of fluoric acid," *Nicholson's J.*, [2], **34**, 81–90 (Feb., 1813); *Phil. Trans.*, **102**, 352–69 (1812).

[23] Obituary notice of John Davy, *Proc. Roy. Soc.* (London), **16**, lxxix–lxxxi (1868).

# A BIBLIOGRAPHY OF CHEMICAL PLANT DESIGN FOR STUDENTS

HELMUT M. HAENDLER AND CHESTER P. BAKER

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THE bibliography was prepared for the use of students in the Chemical Plant Design course at Northeastern University.

No attempt was made to cover all available references on the subject; a representative selection was made from the more common journals, with a few book references. There is necessarily some duplication, certain articles containing material bearing on more than one phase of the plant design problem. The references are arranged in groups, following the customary procedure employed in designing a chemical works. These classifications are: characteristics of the chemical industry, general considerations of the plant design problems, preliminary investigation, technical development—research, semicommercial plant, flow sheets, selection of equipment, materials handling, power factors, plant layouts, plant construction, plant location, plant organization, safety engineering, general economics, and costs. The 194 references are numbered for convenience.

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# *On* CERTAIN CHEMICAL DEFINITIONS

J. K. SENIOR

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OF RECENT years much attention has been given to the problem of devising an accurate and rational terminology for the use of chemists. Unfortunately, however, efforts in this direction have been confined largely to the fixing of names for compounds. Far less attention has been given to the precise definition of ideas, with the result that many statements in some current chemical texts are open to grave objection.

Broadly speaking, two methods for such definition present themselves. A chemical concept may be defined:

(*a*) in terms of verifiable observations and reproducible laboratory operations;

(*b*) in terms of the theory adopted to explain certain phenomena. That is to say, a particular part of chemistry may be defined as the field of application of a given chemical theory.

This paper defends the thesis that the first of these methods is always to be preferred, and that, where theoretical considerations cannot be excluded, their scope is to be limited as strictly as possible. The close connection between this thesis and Bridgman's arguments in favor of "operational" as opposed to "postulated" concepts is obvious.

The reasons for preferring operational definitions are various. In the first place, to define a concept in terms of a theory is, from the pedagogical viewpoint, dangerous. This procedure tends to produce in the mind of the student confusion between phenomena and interpretation—a confusion destructive of almost all sound scientific reasoning. In the second place, if a concept is defined in terms of a theory, any future observation which invalidates the theory at the same time annihilates the concept. If, for instance, Newton had defined "light" in terms of his particular corpuscular theory, Fresnel and Young, when they were led by experiment to abandon this hypothesis, would have had to invent a new terminology. There might have been some question as to what they were talking about, but one thing would have been certain. They would not have been dealing with "light" as previously defined. The tendency of the postulational method to lead to futile wrangling over meaningless questions has been often pointed out.

Although the introduction of postulates into definitions is to be shunned wherever possible, the mention of assumptions previously adopted for use in a wider field is sometimes difficult to avoid. This procedure, though regrettable, is open only to mild objections. But to introduce into a definition an *ad hoc* postulate (that is, one invented for the purpose of explaining the very phenomena under discussion) has such serious drawbacks that it is hard to imagine countervailing advantages sufficient to justify the step.

In this paper no complete analysis of the whole terminology of chemistry is contemplated. An attempt at such an analysis would lead straight to a consideration of the fundamental assumptions on which all scientific theory is based, and would raise psychological and epistemological questions with which the author is incompetent to deal. The problem here proposed is rather the following: Granted the fundamental assumptions which underlie science in general and chemistry in particular, to what extent may the additional concepts useful in special branches of chemistry be defined without introducing additional postulates? And if new postulates must be admitted, how may these be reduced to a minimum? Even the limited program thus indicated cannot, however, be fully carried out within the limits of a single journal article. All that will be here attempted is an analysis of some of the concepts which cluster about the term "isomerism." This theme is chosen not only because of its importance, but because some current chemical texts, in their treatment of this subject, offer fine examples of "how not to do it."

There can scarcely be any dispute that the very idea of isomerism presupposes an adequate scheme of elementary percentual quantitative analysis. If there were (for example) no means of determining when two distinct pure substances have the same per cent. content of carbon, no pair of carbon compounds could be considered isomeric. But furthermore, if there were an adequate percentual analytical scheme, but nothing resembling an atomic-molecular hypothesis, the notion of isomerism could hardly have anything but a vague significance. Under such circumstances, the per cent. compositions of pure substances would be expected to vary continuously. In practice there would be found different samples of material which differed only slightly in their analyses, but there would be great uncertainty as to whether the slight differences observed were significant, or due merely to chance errors—*e. g.*, the presence of small amounts of impurities. An atomic-molecular hypothesis makes the class of all pure substances a discontinuous array, and thus furnishes good grounds for collecting certain sets of slightly divergent analytical results, and regarding their individual items as theoretically identical. Furthermore, such an hypothesis at once suggests the idea of molecular weight and thus indicates the possibility of determining $n$ in an empirical formula $(A_xB_y\ldots)_n$. Isomerism and polymerism are thus distinguished.

If, as has been indicated, the current concept of isomerism depends upon an analytical system and an atomic-molecular hypothesis, then all the postulates (if any) which are necessary for the construction of such a system and such an hypothesis are also implied in the notion of isomerism. But it is significant that no additional assumptions are necessary for the definition of this term. If a certain complex set of observations and operations can be carried out, quantitative analysis and an atomic-molecular hypothesis permit a uniquely determined molecular formula $A_xB_yC_z \ldots$ to be assigned to any pure substance. And when this point has been reached the definition of isomerism follows without further admixture of theory. Isomers are compounds which have identical molecular formulas but which differ in (at least one of) their physical or chemical properties. The all-too-frequent statement that isomers are compounds which have identical molecular formulas but which differ as to the arrangement of the atoms within their respective molecules is logically misleading, pedagogically unsound, and historically false. Such a statement implies the validity of a structural theory, and, as a matter of fact, isomers were known and studied twenty years before any satisfactory structural theory had been devised.

But although isomerism itself may be defined independently of any structural theory, some of the terms applied to special kinds of isomerism are really dependent on such a theory and would be meaningless without it. Stereoisomers, for example, can be defined as isomers which have identical structural formulas. In some instances the differences between their properties are so marked that, without a structural theory, the compounds in question would probably never have been thought of as more closely associated than any ordinary pair of isomers. Here, again, it is all too frequent to meet such statements as the following: "Stereoisomers are isomers which have identical structural formulas but which differ as to the spatial configuration of the atoms composing their respective molecules." This definition implies the validity of some particular subsidiary hypothesis such as the one devised by van't Hoff and Le Bel—a type of hypothesis of which the phenomena to be accounted for are perfectly independent. Unfortunately in this instance, the time interval between the recognition of the phenomena and the publication of a suggested explanation was short, so that no terminology free from theoretical implications ever came into general use. *Stereos* is the Greek word for solid, and it may be urged that, if the van't Hoff (or any similar) hypothesis were to be proven untenable, stereoisomers ought properly to be renamed. However, the bad results which follow from the practice of making the name dependent on the explanation have already been pointed out. In the case of stereoisomerism, these difficulties can be avoided by using the definition suggested. By this means the subject matter is fixed, at least relatively to the structural theory, and the van't Hoff (or any similar) hypothesis is left to stand or fall as experiment may decide.

Enantiomorphism is less easy to define without introducing extra assumptions. Two substances are enantiomorphs if

(*a*) in the fluid phases, under like conditions of concentration, temperature, solvent, etc., they rotate the plane of plane polarized light (of any wave-length) equally but in opposite directions;

(*b*) they react identically toward all chemical reagents which are optically inactive—*i. e.*, do not rotate the plane of polarized light.

The resemblances and differences between the members of a pair of enantiomorphs are so striking that such pairs of compounds could hardly fail to arouse keen interest as soon as they were observed. As a matter of fact, enantiomorphs were identified and investigated by Pasteur quite independently of any structural theory; and it would not even have been necessary for him to appeal to the results of quantitative analysis, though he actually did so. But when it is remembered that only optically inactive reagents are used to determine molecular formulas, it will be seen at once that only isomeric substances can be enantiomorphic. That enantiomorphs must also be stereoisomers follows from the additional fact that the reagents used for the determination of structure almost always are (and in all cases might be) optically inactive. Hence there is experimental justification for speaking of enantiomorphism as a special kind of stereoisomerism. But to define enantiomorphs as substances the molecules of which are non-congruent mirror images of one another is again to base a definition on an explanation—a procedure in this instance both harmful and unnecessary.

Once enantiomorphism has been defined, the definition of diamerism follows by exclusion. Any pair of stereoisomers which is not enantiomorphic is diameric.

Geometric isomerism is a fine example of a term which is not operationally defined—even when the meaning of stereoisomerism is assumed to have been fixed. This particular sort of stereoisomerism is supposed to occur when "free rotation" is hindered or prevented by a double bond, by a ring structure, or by steric hindrance (as in certain terphenyl derivatives, etc.). No definition independent of the *ad hoc* doctrine of free rotation has ever come to the author's attention. And the dangers of the postulational method are well illustrated by the unsatisfactory results which follow from the use of the term in question.

According to current usage, the enantiomorphic forms of 2,2′-dinitrodiphenic acid would not be called geometrical isomers, although the existence of such distinct forms (according to present theories) is dependent on the suppression of the free rotation usually associated with single carbon-to-carbon bonds in open chains. This particular difficulty may be avoided by defining geometrical isomerism as a special form of diamerism, but it is difficult to justify so arbitrary a distinction. Again the meso form of tartaric acid is never called a geometrical isomer of the racemic form, whereas the meso and racemic forms of hexahydrophthalic acid are frequently referred to as *cis* and *trans*. Yet the

analogy between the two pairs is extremely close. Moreover, the term geometrical isomerism not only conceals important resemblances but also ignores profound distinctions. The fact that in ring compounds *cis* and *trans* forms may be identified by so-called "absolute" methods, whereas these methods fail where the isomerism is due to a double bond, indicates that some of the phenomena lumped together under the name of geometrical isomerism are essentially different and probably have little to do with one another. In the opinion of the author, this term is responsible for as much confusion in organic chemistry as has ever been produced by any one word. "Optical isomerism," when used as the antithesis of geometrical isomerism, is naturally open to the same objections. These two terms are not only confusing but superfluous; they should be omitted from the literature.

With regard to "stereochemistry" the situation is even worse. Not only is the ordinary definition postulational rather than operational—but the theory involving the postulates is not even explicitly stated. A well-known textbook (now somewhat out of date) opens with the sentence: "Stereochemistry deals with those chemical and physical phenomena which are believed to be caused by the relative positions in space taken up by the atoms within the molecule." Probably, if the author of this text were to publish a new edition, he would revise his definition and include the relative spatial positions of molecules, so as to bring the subject matter of X-ray crystallography within his field. But the boundaries of stereochemistry as thus defined become indeed vague. For there is no obvious limit to the sort of phenomena which some fervid imagination may attribute to the relative spatial positions of atoms and molecules.

Yet a definition of stereochemistry which implies nothing beyond a structural theory is easily given:

(*a*) On the positive side, stereochemistry deals with those sets of substances which have identical structural formulas but which differ in regard to (at least one of) their physical or chemical properties. That is, it deals with stereoisomers as already defined.

(*b*) On the negative side, stereochemistry attempts to account for the non-occurrence of stereoisomerism among sets of isomers where stereoisomeric forms have never been detected.

It may be objected that stereoisomerism is itself not perfectly defined, since differences of opinion may exist as to whether the members of any given pair of isomers do or do not have the same structural formula. Nevertheless, divergences on such points are rare compared to disagreements as to whether given differences in behavior are or are not due to differences in spatial arrangement. The definition suggested is therefore, if not ideal, at least a great improvement on the one quoted.

Enough has been said to show the urgent need for reconsidering many of the definitions used in current texts and teaching. The author does not claim to be a finished logician, and doubtless some of his suggestions will, for reasons which have escaped him, seem to some of his readers faulty and objectionable. If instances of this kind are called to his attention, he will be grateful.

## A FURTHER NOTE ON DETERMINATION OF EQUIVALENT WEIGHTS

G. O. NESER

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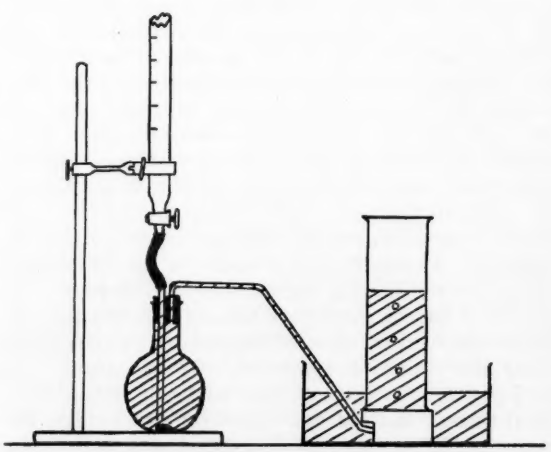
THE article by N. M. Shah [J. CHEM. EDUC., **12**, 492–3 (Oct., 1935)] induced me to send you a diagram of a set-up for determining equivalents, as a laboratory exercise, which we have been using successfully for a number of years.

It combines the psychologically satisfying procedure of actually collecting and measuring the volume of hydrogen liberated—Shah's method I—with the flexibility of his method II.

Light metals are wrapped in copper gauze. Water is run through from the buret to displace all air. Hydrochloric acid is then introduced as required. When necessary, the small flask (100 cc.) can be raised and heated. The glass tubing used has an internal diameter of 2 mm. All gas is finally swept out by a current of water and the usual precautions for levels, temperature, pressure of water vapor, etc., observed.



# REACTIVE GROUPS *in* ORGANIC REAGENTS *and* THEIR APPLICATION *in* INORGANIC ANALYSIS*

LANDON A. SARVER

The University of Minnesota, Minneapolis, Minnesota

ALTHOUGH only a beginning has been made in the use of organic reagents in inorganic analysis, enough has been done to demonstrate their great importance and to indicate in a general way what types of new compounds ought to be prepared and tested in order to advance our knowledge in this direction.

Without such a systematization, the search for new compounds suitable for use as analytical reagents might well appear to be a very baffling, if not hopeless, task. About one thousand research papers have been published on the subject during the past fifty years, a goodly portion of them during the last ten, and more than three hundred such reagents have been proposed. As a result of this work, it is possible to predict with a fair degree of certainty that certain compounds not previously employed will produce precipitates or colored salts with a given metal. It is of course much more difficult to say that a given new reagent will be specific and react with only one metal. In addition to the salt-forming property, the reagent may also have other functions; *e. g.*, it may act as an oxidizing or reducing agent, or it may serve as an indicator. In the present discussion, these latter properties will not be considered.

From the standpoint of structure, there are two fundamental requirements for a good organic analytical reagent. First, with the exception of a few coördinating compounds, they must contain an acidic or salt-forming group in order to react with a metallic ion (7). The most important of these are: (1) the imino, or =NH group; (2) the oxime, or =NOH group; (3) the hydroxyl, or —OH group; and (4) the mercapto, or —SH group. The carboxyl, or —COOH group, and the sulfonic acid, or —$SO_3H$ group, have been of little importance so far, although they have been employed. In addition, any compound which is capable of forming one of the above groups by molecular rearrangement must be considered. In each case, the hydrogen of the acidic group is replaced by one equivalent of metal whenever other conditions are favorable to the formation of an insoluble or undissociated salt.

The second fundamental requirement is that the molecular structure of the reagent must be such as to make possible the formation of a ring containing the metal (*18*), usually by means of one electrovalent link and one coördinate valence, although this is not absolutely essential, and either two electrovalences or two coördinate valences may be employed. It is true that organometallic compounds are known in which there appears to be no chelate ring containing the metal, but from the analytical point of view ring formation seems to be an absolute requirement. In those cases where coördinate valences are required to complete the ring, the metal is most often attached in this way to nitrogen, but also frequently to sulfur or oxygen.

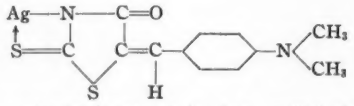
In the design and synthesis of a new reagent, Baeyer's strain theory is frequently of great assistance, although the laws concerning strain are not yet known with sufficient accuracy to make predictions with absolute certainty. It can be said, in a qualitative way at least, that the most stable rings are those containing six members and two double bonds, and those with five members and no double bonds. A six-membered ring with one double bond should be somewhat more stable than a five-membered ring with one double bond and considerably more stable than a six-membered ring with no double bond. In accordance with the theory, the great majority of known reagents give chelate rings containing five or six atoms; a smaller number give salts with four-membered rings, while three-, seven- and eight-membered rings are very rare. When two or more of the atoms of a chelate ring also form part of an unsaturated aromatic ring, it can be assumed that a double bond is or is not present, according to the requirements for the formation of a stable compound.

### THE IMINO GROUP

Numerous substances containing the imino, or =NH group, are capable of reacting with certain metals, especially silver, mercury, gold, platinum, palladium, and copper. Examples of these are rhodanine and its derivatives. By the introduction of suitable chromophoric groups into the molecule the resulting salts may be given a color, and the usefulness of the reagents thereby greatly increased. Thus, 5-(*p*-dimethylaminobenzal)rhodanine (*8*) gives a reddish violet silver salt which is insoluble in dilute acid solutions (Figure 1). The precipitation of mercury, gold, etc., may be pre-

* Contribution to the symposium on Organic Analytical Reagents conducted by the Division of Physical and Inorganic Chemistry at the ninety-first meeting of the American Chemical Society, Kansas City, April 16, 1936.

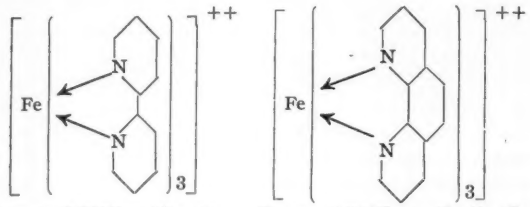
vented by the presence of cyanide, so that under these conditions the reagent serves as a specific precipitant for silver. It will be noted that the metal becomes part of a four-membered ring (along with nitrogen, carbon, and sulfur) with one double bond; it is attached to the nitrogen by an ordinary bond, and to the sulfur by a coördinate valence.



Silver salt of 5-(*p*-dimethylaminobenzal)rhodanine

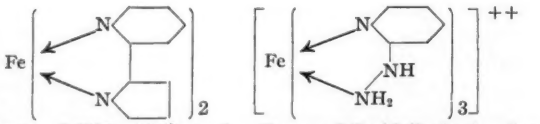
FIGURE 1

It should be remarked in this connection that the nitrogen of pyridine behaves like an imino group, and forms coördination compounds with certain metals (Figure 2). Thus, ferrous iron reacts in a specific way with 2,2′-bipyridine, and 1,10-phenanthroline to give intensely red complex ions which are very stable in the presence of mineral acids, and against oxidation by the air (*4*). The very similar 2-(2′-pyridyl)pyrrole and 2-pyridylhydrazine also give colored complex ions with ferrous iron, but these are less stable in the presence of acids and against oxidation by the air (*5*).



Ferrous 2,2′-Bipyridine Ion I

Ferrous 1,10-Phenanthroline Ion II



Ferrous 2-(2′-Pyridyl)pyrrole III

Ferrous 2-Pyridylhydrazine Ion IV

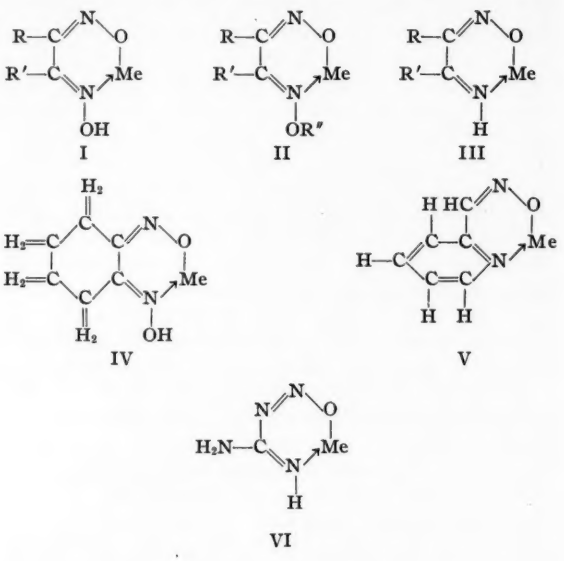
FIGURE 2

In each of these examples, the iron forms part of a five-membered ring with no double bonds—a very stable configuration, according to the strain theory of Baeyer. They emphasize two facts: first, nitrogen and carbon atoms are interchangeable (*cf.* 2-pyridylhydrazine), both possessing a tetrahedral symmetry; second, coördinate links are no less genuine than ordinary valences, and they are interchangeable with normal ones with regard to the strain produced in the ring. The two kinds of bonds differ only in the fact that in an ordinary linkage one of the shared electrons is contributed by each of the atoms, while in a coördinate linkage both electrons come from the same atom, in this case the nitrogen.

### THE OXIME GROUP

The oximes have been the most fully investigated of all the organic analytical reagents, and more than sixty are known. They react generally with iron, cobalt, nickel, copper, platinum, palladium, and a few other metals. Indeed, some oximes precipitate almost all the metals, and thus lose their chief value as analytical reagents, since highly specific precipitants are the most to be desired. But certain ones react with a single metal under suitable conditions.

Dimethylglyoxime is probably the best known organic analytical reagent, and has been used for separating nickel from cobalt since 1905 (*20*). Not only this, but other $\alpha$-dioximes of the same general type (Figure 3) yield colored precipitates, usually red, with nickel salts (*15*). Either alkyl or aryl groups may replace the R, R′, and R″ in formulas I, II, and III, and the compound may be either symmetrical or unsymmetrical.



Metallic Salts of Dioximes and Related Compounds

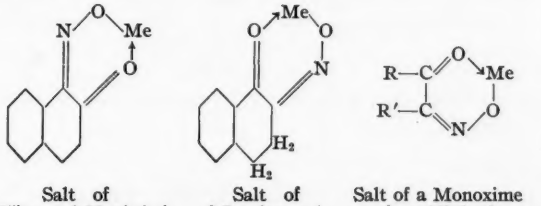
FIGURE 3

The hydrogen of one of the oxime groups may be replaced by an organic radical (*14*), or the entire group may be replaced by an imino group without loss of its characteristic nickel-precipitating properties, as in formulas II and III, respectively; indeed the nitrogen of a pyridine ring may serve just as well as the second group, as in formula V (*5*, *20*). Two aliphatic carbon atoms are present in most of the reagents thus far investigated, but this is not a necessary requirement, and one of them may form part of an unsaturated ring along with one of the nitrogens, as in 2-pyridylformaldoxime (formula V) (*5*); or both of them may occur

in a saturated ring, as in 1,2-cyclohexadione dioxime (formula IV) (*22*). The interchangeability of carbon and nitrogen atoms is shown again in the nickel salt of nitrosoguanidine (Formula VI) (*21*), where there are three nitrogens and one carbon instead of the usual ring with two nitrogens and two carbons. All of these compounds act as monobasic acids and react with only one equivalent of metal, although many of them might be expected to be dibasic.

Thus, we see that the salts of all compounds of this class possess a six-membered chelate ring consisting of the metal, one oxygen, and four nitrogen or carbon atoms, with two double bonds. According to Pfeiffer (*14*), the oxygen does not form part of the ring, in which case there would be only a five-membered ring with two double bonds; however, if we accept the strain theory of Baeyer, we should expect a six-membered ring, since it is much more stable.

Compounds which have an oxime and a keto group attached to the same carbon atom react generally with ferrous iron to give deep-blue water-soluble chelate compounds which are soluble in organic solvents (*23*). In addition, they usually give green colors with ferric iron, and red precipitates with cobalt. The best-known example of this class of substances is 1-nitroso-2-naphthol, proposed by Ilinsky and von Knorre in 1885 for the separation of cobalt from iron and nickel (Figure 4) (*13*). These compounds exist in equilibrium with the corresponding oximes, and their salts have chelate rings similar to those obtained with the dioximes, except that one of the nitrogens has been replaced by an oxygen. The carbon atoms may be aliphatic in nature, as in $\alpha$-benzil monoxime; or they may form part of an aromatic ring, provided that the latter is not completely saturated, as in 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, or 2-isonitroso-1-ketotetralin (*19*). In each case, there is a six-membered chelate ring, with two double bonds. These substances are used principally as reagents for cobalt and iron.



Salt of 1-Nitroso-2-Naphthol — I

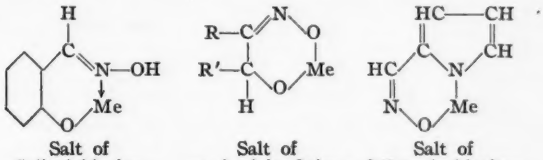
Salt of 2-Isonitroso-1-ketotetralin — II

Salt of a Monoxime of an Aliphatic Dicarbonyl Compound — III

FIGURE 4

Monoximes which have a hydroxyl group on the second or third carbon atom (Figure 5) act as specific precipitants for copper, giving green salts which are insoluble in water; most of them are also insoluble in aqueous ammonia. Salicylaldoxime and its analogs, fifteen of which have been examined (*6*), react as monobasic acids, the hydrogen of the hydroxyl group only being replaced by an equivalent of the metal, as shown by the behavior of the two isomeric methyl ethers; thus, the hydroxyl and not the oxime is the salt-forming group in this case. Again, the chelate rings consist of six atoms, with two double bonds.

The situation is somewhat different, however, with $\alpha$ benzoin oxime and its analogs, twenty-two of which have been examined (*11*). They act as dibasic acids, and give six-membered rings with only one double bond, the divalent metal being linked by two normal covalences instead of by one normal and one coördinate valence, as in the other classes of oximes previously mentioned. Variation of R and R′ has no effect upon the insolubility of the cupric salts in water, but does have an influence upon their solubility in ammonia; they appear to be insoluble in the latter when the substituted groups are able to satisfy the coördination valences of the metal. There is no distinction between the symmetric and the unsymmetric compounds. Aromatic radicals cause insolubility in all cases, except where two of them are attached to the same carbon atom as the hydroxyl, as in $\alpha$-phenylbenzoin oxime or $\alpha$-benzylbenzoin oxime. An amino group has the same effect as a phenyl; and compounds having alkyl groups of four or more carbon atoms give copper salts insoluble in ammonia, while those with smaller alkyl groups are soluble. It is interesting to note that 2-pyrrolealdoxime (*5*, *12*) also gives an insoluble copper salt having a six-membered chelate ring, with one double bond, where the oxygen atom of the usual hydroxyl group has been replaced by the nitrogen of the pyrrole ring.



Salt of Salicylaldoxime — I

Salt of an Acyloin Oxime — II

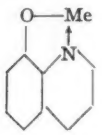
Salt of 2-Pyrrolealdoxime — III

FIGURE 5

## THE HYDROXY GROUP

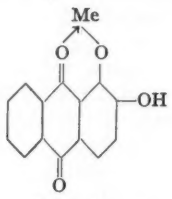
Some hydroxy compounds have already been discussed in connection with the oximes; there are in addition a number of other types, such as 8-quinolinol (8-hydroxyquinoline), the hydroxyanthraquinones, the enolizable ketones and diketones, and the arsonic acids (Figure 6). 8-Quinolinol (*1*) and its derivatives are unusually active reagents, forming salts with a large number of metals. They have five-membered chelate rings, with no double bonds, which constitute one of the most stable possible configurations. The hydroxyanthraquinones, on the other hand, give salts with aluminum, chromium, iron, beryllium, magnesium, calcium, strontium, barium, zirconium, etc., which have six-membered chelate rings, with one double bond, and may be expected to be rather

stable, but less so than the salts of 8-quinolinol. Enolizable $\beta$-diketones give a highly specific but insensitive reaction with thallium in the presence of carbon disulfide; if only one ketone group is enolizable, a monothallium salt is obtained, but no reaction with carbon disulfide (*9*). In each case, six-membered chelate rings, with two double bonds, are obtained. The arsonic acids are used as precipitants for zirconium (*10*, *17*) and give four-membered rings; if the metal also links itself with the doubly bound oxygen by a coördinate valence, there is one double bond in the ring; otherwise it has only normal covalences.



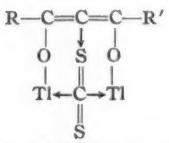
Salt of 8-Quinolinol (8-Hydroxyquinoline)

I



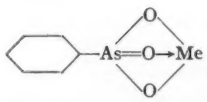
Salt of a Hydroxyanthraquinone

II



Carbon Disulfide Complex with a Dithallium Salt of an Enolizable $\beta$-Diketone

III



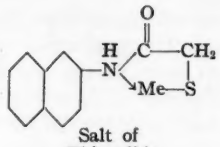
Salt of Phenylarsonic Acid

IV

FIGURE 6

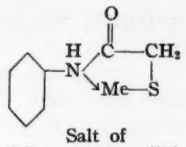
## THE MERCAPTO GROUP

The mercapto group is extremely active, and the analytical properties of a number of such reagents have already been studied; *e. g.*, thionalide (*2*), mercaptoacetanilide (thioglycollic acid anilide) (*3*), 8-quinolinethiol (8-mercaptoquinoline), rubeanic acid (*16*), and "phenylthiohydantoic acid"(*24*). All of the compounds mentioned give metallic derivatives having five-membered chelate rings, with no double bonds (Figure 7).



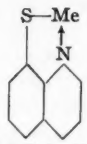
Salt of Thionalide

I



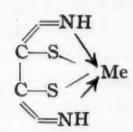
Salt of Mercaptoacetanilide

II



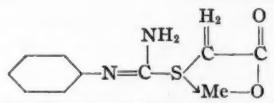
Salt of 8-Quinolinethiol

II



Salt of Rubeanic Acid

IV



Salt of "Phenylthiohydantoic Acid"

V

FIGURE 7

## CONCLUSION

It is evident from the foregoing examples that a given organic compound may be expected to prove useful as an analytical reagent if it is able to unite with a metal by virtue of an acidic group (such as an imino, oxime, hydroxyl, mercapto, or carboxyl group), and if it is also possible to form a ring of four, five, or six atoms, with or without double bonds. The nature of the non-metallic atoms in the ring appears to be unimportant, but they are most frequently carbon, nitrogen, oxygen, or sulfur. The metal is almost always attached to a nitrogen, oxygen, or sulfur atom by a normal covalence, very rarely directly to carbon. The ring is usually closed by means of a coördinate valence from the metal to a nitrogen, oxygen, or sulfur atom, rarely to carbon; however, it may also be closed by another normal covalence. In rare cases two coördinate valences may complete a ring. While the laws of chemical combination are not yet known with sufficient certainty to make accurate predictions in all cases, the application of these principles will surely be of great assistance in the search for new organic analytical reagents.

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# IMPROVED SODIUM FUSION TECHNIC *for* VOLATILE *or* DIFFICULTLY DECOMPOSABLE LIQUIDS

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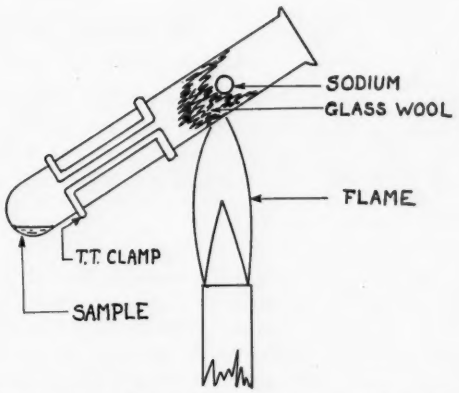
A COMPARATIVE study of the currently accepted methods for making sodium fusions and a new modified method has been made. The points compared were relative safety and relative sensitivity. Houben (*1*) points out that for volatile liquids, better results are obtained by using potassium metal in place of sodium. The modification here suggested makes this substitution unnecessary. Two technics are recorded in standard reference books; *Chemical Abstracts* lists separately no sodium fusion method during the years 1907–1935 inclusive. One method consists in placing the sodium and the sample together before heating (*1*, *2*, *3*, *4*). The other requires that the sodium be first heated to redness and the sample then dropped upon it (*5*, *6*). Both of these methods, particularly the latter, produce disagreeably violent reactions. However, since the latter gave consistently stronger tests, it was used for comparison.

The proposed method consists essentially in passing the vapors of the organic compound (or its decomposition products) over red-hot sodium, insuring a maximum of conversion and also permitting, to a certain degree, control of the speed and thus the vigor of the reaction. The scheme is illustrated by the accompanying diagram.

The sample is placed at the bottom of a four-inch soft glass test-tube,† a plug of glass wool is placed somewhat above the center of the tube and the sodium is placed thereon. The sodium is heated. In the case of very volatile compounds, enough heat reaches the sample to vaporize it. The vapor passes over the hot sodium causing it to glow more brilliantly as it reacts. In other cases, it is necessary to shift the test-tube forward and backward, heating both sodium and sample. A few trials will serve better than any further hints.

In order to satisfy ourselves that this method would not lead beginners astray were solids to be used (and this method is not necessary with solids), we made a few trials on solids. Then to prove the safety of the method we used aqueous solutions. Typical data are tabulated.




ILLUSTRATING SODIUM FUSIONS BY THE MODIFIED METHOD

TABLE

| COMPOUND | OLD METHOD (KAMM) | NEW METHOD |
|---|---|---|
| *Liquids* | | |
| Chlorobenzene | + | + |
| Acetonitrile | + | ++ |
| Carbon disulfide | + | +++ |
| Carbon tetrachloride | + | ++ |
| Nitrobenzene | + | ++ |
| Ethyl bromide | + | +++ |
| Ethyl chloride | + | +++ |
| *Solids* | | |
| Hippuric acid | + | + |
| *Aqueous solutions* | | |
| 10% acetonitrile | (not attempted) | + |

where + = distinct precipitate
++ = copious precipitate
+++ = very copious precipitate

In conclusion may we generalize only to this extent: the new method gives consistently positive results which tend to be stronger than those of the older methods, especially for very volatile liquids; the new method allows for a degree of control over the speed of the reaction, increasing safety, as evidenced by the feasibility of carrying out a fusion in aqueous solution.

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* Graduate teaching assistant, Wayne University, 1935–36.

† It is not necessary to use pyrex test-tubes, for should the test-tube crack, the glass wool holds the parts together sufficiently well to permit the fusion to go on.

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# SIMPLER ASPECTS *of* ELECTROCHEMISTRY

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*An introduction to electrochemistry with a minimum of mathematics suitable for elementary students is presented. The electromotive series secured by compiling standard electrode potentials is stressed and a modified list of potentials is used to illustrate the prediction of the products of electrolysis of a given solution. The "secondary action" concept in interpreting electrolysis is shown to be not only unnecessary, but highly improbable.*

✦ ✦ ✦ ✦ ✦ ✦

A VOLTAIC cell may be thought of as a system in which two parts of a spontaneous reaction (of the type which consists of a transfer of electrons from one substance to another) are separated so that the electrons must flow along a wire in order to reach their destination. This flow of electrons along the wire represents an electric current, and may be made to do useful work. The voltaic cell, then, is an arrangement for converting the energy of a chemical reaction into electricity.

The electrolytic cell, on the other hand, makes use of a flow of electrons, produced externally, to force a desired chemical change to take place, the latter usually being one which is not spontaneous, or ordinarily proceeds in the reverse direction. Examples of this use would be electrolysis of water to yield hydrogen and oxygen, electroplating of metals, preparation of chlorine and sodium hydroxide from brine, and many others of a similar nature. The fact that water does not decompose to form hydrogen and oxygen spontaneously, although the combination of hydrogen and oxygen proceeds explosively when once started, illustrates the reversal principle here. In fact, a reaction which proceeds spontaneously does not need the action of an outside agent such as electricity to force the reaction, but, instead, may be used to produce a current.

An example of a spontaneous reaction which may be used to generate a current is that between zinc metal and cupric sulfate solution. It is a well-known fact that a strip of metallic zinc placed in a solution of cupric sulfate or other cupric salt rapidly dissolves, while metallic copper is deposited loosely on the zinc. According to our present knowledge, this is due to electrons leaving the metallic zinc to form $Zn^{++}$ ions and going to the $Cu^{++}$ ions to form metallic copper, whose ions have a greater attraction for electrons than those of zinc:

$$Zn^0 \rightarrow Zn^{++} + 2e$$
$$2e + Cu^{++} \rightarrow Cu^0$$

To make a voltaic cell from this reaction it is necessary to separate the metallic zinc from the $Cu^{++}$ ions so that the electrons cannot leave the zinc and unite directly with the $Cu^{++}$ ions, but must flow along a wire to reach them. This is done by placing a zinc electrode in a solution of $ZnSO_4$ which is in contact, but not mixed, with a solution of $CuSO_4$ which contains a copper electrode. Such an arrangement is called the Daniell cell. When the two electrodes are joined by a wire, electrons begin to flow from the zinc to the copper along the wire, while the current is carried in the solutions by ions, to complete the circuit. The number of $Zn^{++}$ ions will increase while copper metal will plate on the copper electrode, thus decreasing the number of $Cu^{++}$ ions. The total number of positive ions will remain constant, and they are free to move, as are the $SO_4^{--}$ ions, so that the electrical balance is maintained. However, mixing of the $Cu^{++}$ and $Zn^{++}$ ions gradually destroys the cell since it brings $Cu^{++}$ ions in direct contact with the zinc metal.

The electromotive force of such a cell may be accurately measured and is found to have a definite value depending on the temperature and the concentration of the solutions. This measurable E.M.F. is really the sum of the potential differences which are found wherever there is a junction of two different phases of the cell, *i. e.*, the point of contact of the electrode and its solution, the contact of the two liquids, the joining of the wires to the electrodes, etc. It has been customary to disregard all these potential differences except those where the electrode comes into contact with the solution con-

taining its ions. What really happens is that they are included in the value used for this potential and, as long as the values used are consistent, this introduces no error. The total E.M.F. for the cell may be thought of as the sum of the potential differences between the cupric sulfate and copper ($E_{Cu^{++},\ Cu^0}$) and zinc and zinc sulfate ($E_{Zn^0,\ Zn^{++}}$). Some authors write it as the difference between $E_{Zn^0,\ Zn^{++}}$ and $E_{Cu^0,\ Cu^{++}}$. Obviously, the single potential for Cu, $Cu^{++}$ has the same numerical value (though the opposite sign) as that for $Cu^{++}$, Cu. In accordance with the convention adopted by Lewis and Randall[1] for the process Cu(s), $Cu^{++}$ the potential is negative, while that for $Cu^{++}$, Cu(s) is positive, the latter being in general the more spontaneous.

The single-electrode potential, like the E.M.F., is a definite value dependent on the concentration, the temperature, and, of course, on the nature of the ions. It may be expressed mathematically as:[2]

$$E = E_0 - \frac{RT}{NF} \ln \frac{a''}{a'}$$

where $E_0$ is constant for the metal and is known as the standard electrode potential, $R$ is the gas constant per gram mole (1.985 × 4.184 joules), $T$ = absolute temperature, $N$ = number of electrons involved, $F$ is the Faraday (96,500 coulombs) and $a''$ equals the activity of the final state while $a'$ represents the activity of the initial state. By activity is meant the apparent or effective concentration, which corresponds roughly to the per cent. ionization times molality. Substituting these values, changing the natural logarithms to the base 10, and assuming a temperature of 25°C. or 298°A., we arrive at the equation:

$$E = E_0 - \frac{0.05915}{N} \log \frac{a''}{a'}.$$

Some authors, by a different convention, get opposite signs in this equation; or the initial activity over the final activity will give the opposite sign. If the initial or final state is solid, or a gas at one atmosphere pressure, the activity is taken as unity. If the initial state happens to be solid its activity becomes unity and that term may be dropped from the equation, which now becomes:

$$E = E_0 - \frac{0.05915}{N} \log a''$$

but if the final state is solid, the equation becomes:

$$E = E_0 - \frac{0.05915}{N} \log \frac{1}{a'}$$

which might also be written:

$$E = E_0 + \frac{0.05915}{N} \log a'$$

since $\log \frac{1}{a'} = -\log a'$.

If the solution in the cell has a concentration such that its activity is unity, the whole expression $\frac{0.05915}{N}$ $\log a'$ becomes equal to zero since $\log 1 = 0$, and $E$ now becomes equal to $E_0$, which as stated above is known as the standard electrode potential. Some gases, notably hydrogen, may also be kept in contact with their ions and so produce a definite electrode potential. Spongy platinum absorbs hydrogen gas and acts as though it were a solid electrode of hydrogen. The sum of the potentials of the cell may be easily determined experimentally, but it is impossible to determine the absolute value of any one. It is necessary, therefore, to assign some value arbitrarily to one electrode and calculate the others by reference. This is a very common principle in science, in fact, in everyday life, as there are very few things the absolute values of which are known. It has been agreed to assign to $E_0$ for the system Pt, $H_2$, $H^+$ the value zero, and since these values are reversible, $E_0$ for $H^+$, $H_2$, Pt, is also zero. The electrode which has this value consists of platinized platinum with hydrogen gas at 1 atmosphere pressure in a solution containing an effective concentration of 1 gram ion of $H^+$ ion per liter of solvent. This gives it an activity of 1. A cell consisting of this standard electrode and some other electrode, the value of which is to be determined, is then made, care being taken to eliminate all sources of error. From the resulting voltage, very accurately measured, the potential for the unknown electrode may be calculated. From this and other potentials so determined the potentials of still more electrodes are found. Due to the great difficulty in eliminating all sources of error, only relatively few values are known with any degree of certainty. Perhaps the most accurate work in this field has been done by Lewis and Randall. This work has resulted in the following set of standard electrode potentials:[3]

TABLE 1

STANDARD ELECTRODE POTENTIALS AT 25°C.

Part I (Lewis and Randall)

| | *Electrode* | $E_0$ | | *Electrode* | $E_0$ |
|---|---|---|---|---|---|
| 1. | Li, $Li^+$ | 2.9578 | 11. | Fe, $Fe^{+++}$ | 0.045 |
| 2. | Rb, $Rb^+$ | 2.9242 | 12. | Pt, $H_2$, $H^+$ | 0.000 |
| 3. | K, $K^+$ | 2.9224 | 13. | Cu, $Cu^{++}$ | −0.3448 |
| 4. | Na, $Na^+$ | 2.7125 | 14. | Pt, $OH^-$, $O_2$ | −0.3976 |
| 5. | Zn, $Zn^{++}$ | 0.7581 | 15. | Pt, $I^-$, $I_2$(s) | −0.5357 |
| 6. | Pt, $S^{--}$, S(r) | 0.51 | 16. | Hg, $Hg_2^{++}$ | −0.7986 |
| 7. | Fe, $Fe^{++}$ | 0.441 | 17. | Ag, $Ag^+$ | −0.7995 |
| 8. | Cd, $Cd^{++}$ | 0.3976 | 18. | Pt, $Br^-$, $Br_2$(l) | −1.0659 |
| 9. | Sn, $Sn^{++}$ | 0.136 | 19. | Pt, $Cl^-$, $Cl_2$(g) | −1.3594 |
| 10. | Pb, $Pb^{++}$ | 0.122 | | | |

Part II (Abegg, Auerbach, and Luther)*

| | *Electrode* | $E_0$ | | *Electrode* | $E_0$ |
|---|---|---|---|---|---|
| 1. | Ba, $Ba^{++}$ | 2.8 | 8. | Ni, $Ni^{++}$ | 0.22 |
| 2. | Sr, $Sr^{++}$ | 2.7 | 9. | Sb, $Sb^{+++}$ | −0.1 |
| 3. | Ca, $Ca^{++}$ | 2.5 | 10. | Bi, $Bi^{+++}$ | −0.2 |
| 4. | Mg, $Mg^{++}$ | 1.55 | 11. | As, $As^{+++}$ | −0.3 |
| 5. | Mn, $Mn^{++}$ | 1.0 | 12. | Au, $Au^+$ | −1.5 |
| 6. | Cr, $Cr^{+++}$ | 0.5 | 13. | Pt, $F^-$, $F_2$(g) | −1.9 |
| 7. | Co, $Co^{++}$ | 0.29 | | | |

* The values in the second list, which Taylor has taken from Abegg, Auerbach, and Luther, are of a lower degree of accuracy than those in Part I.

[1] LEWIS, G. N. AND RANDALL, M., "Thermodynamics and the free energy of chemical substances," 1st ed., McGraw-Hill Book Co., Inc., New York City, 1923, pp. 389 and 402.

[2] LEWIS, G. N. AND RANDALL, M., *loc. cit.*, p. 403.

[3] TAYLOR, H. S., "A treatise on physical chemistry," Vol. 1. D. Van Nostrand Company, New York City, 1931, pp. 827–8.

Returning to a discussion of the Daniell cell, we have for Zn, $Zn^{++}$: $E = 0.7581 - \frac{0.05915}{2} \log a_{Zn^{++}}$. Using molal solutions and considering the $Zn^{++}$ ion to have an activity coefficient of about 0.5, $E = 0.7581 - 0.0295 \log 0.5$. Since the log 0.5 = approximately $-0.3$, $E = 0.7581 + 0.0088 = 0.7668$. The value is positive because the reaction in the cell proceeds in the same direction as that for the standard potential as taken from the table. Similarly, for Cu we have $E = 0.3448 - 0.295 \log \frac{1}{a_{Cu^{++}}}$ since for this electrode the true action is the reverse of that in the table requiring us to reverse the sign of the potential and use the expression $\log \frac{1}{a}$ because $Cu^{++}$ ion represents the initial state and Cu metal the final. Again assuming an activity of 0.5 for the $Cu^{++}$ ion, it is seen that the expression reads $\log \frac{1}{0.5}$, which equals $-\log 0.5$ or $+0.3$. $E_{Cu^{++},\,Cu^0} = 0.3448 - 0.0088$, which equals 0.3360. The same result could have been obtained by reversing the sign of the value of $E_{Cu^{++},\,Cu^0}$. Adding these two values, the result 1.10 volts is obtained, which agrees fairly well with the value experimentally determined for the Daniell cell under these conditions.

By the addition algebraically, then, of any two sets of single electrode potentials corrected for temperature, concentration, and other effects to be discussed later it is possible to calculate the voltage which the corresponding cell will develop. It is obvious that the farther apart the metals used as electrodes are, in the table, the more voltage one can obtain. It is important here to remember that the sign of the partial voltages must be determined from a study of the direction in which the reaction proceeds. For example, the potential for K, $K^+$ is highly positive since the solution of metallic K represents a vigorous spontaneous reaction while the potential for $K^+$, K has the same numerical value, but a negative sign since a high potential must be applied in order to discharge potassium from its solutions.

Applying these principles, it is seen that an electrode reaction which proceeds readily and spontaneously in one direction, producing a certain positive potential, will require the *application* of an equal potential to effect equilibrium, and the potential must be slightly exceeded for it to proceed in the reverse direction.

Referring to the list of potentials, it is found that the numerical values of those of the cations and of the anions are in the same range. For example, sulfur is placed between zinc and iron because the potential for the system $S^{--}$, S(rhombic) is $+0.51$, while that for Zn, $Zn^{++}$ is $+0.7581$ and for Fe, $Fe^{++}$ is $+0.441$. It is to be noted here that while the anion changes to the free state, the metallic element changes to the ionic condition.

One finds lithium metal changing to $Li^+$ ion at the top and the $F^-$ ion changing to gaseous fluorine at the bottom. The anomaly of placing the most active nonmetal at the inactive end of the series is easily explained by the fact that it is the $F^-$ ion which is so placed and not the element fluorine. The fluoride ion is truly inactive in the sense considered here, since electrons are removed from the $F^-$ ion only with the greatest difficulty. The reaction in every case, as previously mentioned, represents loss of electrons, the higher ones undergoing the reaction resulting in this loss with the greatest ease and the lower ones with the greatest difficulty. In the reverse process, in which, *e. g.*, a $Li^+$ ion is changed to the metal and fluorine gas to the $F^-$ ion, the higher ones undergo the reaction with the greatest difficulty while the lower ones (*e. g.*, chlorine and fluorine) react with the greatest ease. It is to be noted here that the sign of the potential is in each case the reverse of that when electrons are lost.

In electrolysis, using inert electrodes, all the elements or groups involved in the electrolysis are present in the ionic state, at first, and the passage of the electric current adds electrons to the cations to give the corresponding free element and removes electrons from anions to give the free electronegative element. For clarity of teaching it is probably best to use a chart containing the cations and anions in two parallel columns. The cation list should start with lithium and the anion list with fluorine. These two elements, while chemically opposite, are alike in that they both prefer the ionic state and are difficult to obtain in elementary form.

TABLE 2

DISCHARGE OF IONS BY ELECTROLYSIS

Ions at top difficult to discharge (prefer ionic state)

| CATIONS | | ANIONS | |
|---|---|---|---|
| *Electrode reaction* | $E_0$ | *Electrode reaction* | $E_0$ |
| 1. $Li^+ + e \rightarrow Li$ | $-2.9578$ | 1. $2F^- \rightarrow F_2 + 2e$ | $-1.9$ |
| 2. $Rb^+ + e \rightarrow Rb$ | $-2.9242$ | | |
| 3. $K^+ + e \rightarrow K$ | $-2.9224$ | 2. $PO_4^{---}$ rarely, | estimated |
| 4. $Ba^{++} + 2e \rightarrow Ba$ | $-2.8$ | 3. $NO_3^-$ if ever, | about |
| 5. $Na^+ + e \rightarrow Na$ | $-2.7125$ | 4. $SO_4^{--}$ discharged | $-2.0$ |
| 6. $Sr^{++} + 2e \rightarrow Sr$ | $-2.7$ | 5. $ClO_4^-$ | |
| 7. $Ca^{++} + 2e \rightarrow Ca$ | $-2.5$ | 6. $2Cl^- \rightarrow Cl_2 + 2e$ | $-1.3594$ |
| 8. $Mg^{++} + 2e \rightarrow Mg$ | $-1.55$ | 7. $2Br^- \rightarrow Br_2 + 2e$ | $-1.0659$ |
| 9. $Mn^{++} + 2e \rightarrow Mn$ | $-1.0$ | 8. $2I^- \rightarrow I_2 + 2e$ | $-0.5357$ |
| 10. $Zn^{++} + 2e \rightarrow Zn$ | $-0.7581$ | 9. $4(OH^-) \rightarrow O_2 +$ | |
| 11. $Cr^{+++} + 3e \rightarrow Cr$ | $-0.5$ | $2H_2O + 4e$ | $-0.3976$ |
| 12. $Fe^{++} + 2e \rightarrow Fe$ | $-0.441$ | 10. $S^{--} \rightarrow S + 2e$ | $+0.51$ |
| 13. $Cd^{++} + 2e \rightarrow Cd$ | $-0.3976$ | | |
| 14. $Co^{++} + 2e \rightarrow Co$ | $-0.29$ | | |
| 15. $Ni^{++} + 2e \rightarrow Ni$ | $-0.22$ | | |
| 16. $Sn^{++} + 2e \rightarrow Sn$ | $-0.136$ | | |
| 17. $Pb^{++} + 2e \rightarrow Pb$ | $-0.122$ | | |
| 18. $2H^+ + 2e \rightarrow H_2$ | $0.0000$ | | |
| 19. $Sb^{+++} + 3e \rightarrow Sb$ | $+0.1$ | | |
| 20. $Bi^{+++} + 3e \rightarrow Bi$ | $+0.2$ | | |
| 21. $As^{+++} + 3e \rightarrow As$ | $+0.3$ | | |
| 22. $Cu^{++} + 2e \rightarrow Cu$ | $+0.3448$ | | |
| 23. $Hg_2^{++} + 2e \rightarrow 2Hg$ | $+0.7986$ | | |
| 24. $Ag^+ + e \rightarrow Ag$ | $+0.7995$ | | |
| 25. $Au^+ + e \rightarrow Au$ | $+1.5$ | | |

There are a number of complications which are likely to enter into any attempt to predict the result of the passage of an electric current through a solution, especially when there is more than one positive or negative ion present. It is not possible to say that certain things will happen if electricity is passed through a solution. It is necessary, as has been mentioned, to know the current density and the voltage applied. At a low current density (measured in amperes per square

centimeter, or other similar units) cupric solutions require a higher potential for deposition than with a higher current density. However, the variation is less than for some other metals, especially those of the iron group.[4]

TABLE 3

CATHODE POTENTIALS OF METALS AT DIFFERENT CURRENT DENSITIES

| *Current Density* ($\frac{10^{-4}\ \text{amperes}}{\text{cm.}^2}$) | *Cathode Potentials* | | | |
|---|---|---|---|---|
| | $CuSO_4$ | $FeSO_4$ | $NiSO_4$ | $CoCl_2$ |
| 0 | −0.303 | 0.465 | (0.220) | 0.290 |
| 1 | −0.294 | 0.580 | 0.445 | 0.370 |
| 5 | −0.285 | 0.619 | 0.524 | 0.415 |
| 10 | −0.275 | 0.630 | 0.546 | 0.430 |
| 20 | −0.270 | 0.645 | 0.559 | 0.440 |
| 40 | −0.260 | ... | 0.570 | 0.459 |
| 80 | −0.240 | ... | 0.590 | 0.495 |

The rapid flow of electricity may deplete the solution of certain ions in the neighborhood of the electrode and hence lead to a different potential and the deposition or solution of another substance. This is known as polarization, which may be thought of as any change produced at the electrode by electrolysis or by some other means which causes its potential to differ from the normal value. This may in some measure be eliminated by stirring the solution and thus preventing changes in concentration. It is true, however, that as electrolysis proceeds the concentration of the ions being discharged will decrease unless they are being added in some way. This will produce a change in the products being discharged. The application of a voltage greatly in excess of that required for electrolysis also increases the current density and so leads to the effects just mentioned. The value of zero given for the reversible standard electrode potential for hydrogen is that for hydrogen gas in contact with platinized platinum (also known as spongy platinum). For smooth platinum and other metals an additional potential must be applied beyond the reversible value before hydrogen gas is evolved. This additional voltage is known as the overvoltage of hydrogen and is also found in the case of other gases. While this is small in the case of smooth platinum, it reaches rather high values in the case of some other metals, and especially zinc.[5]

TABLE 4

HYDROGEN OVERVOLTAGE OF ELEMENTS

| *Element* | *Overvoltage* | *Element* | *Overvoltage* |
|---|---|---|---|
| Cu | 0.34 | Pb | 0.42 |
| Ag | 0.30 | Fe | 0.27 |
| Mg | 0.70 | Ni | 0.24 |
| Zn | 0.72 | Pt | 0.18 |
| Al | 0.50 | | |

TABLE 5[6]

OXYGEN OVERVOLTAGE OF ELEMENTS

| *Metal* | *Overvoltage* | *Metal* | *Overvoltage* |
|---|---|---|---|
| Cu | 0.62 | Co | 0.55 |
| Ag | 0.71 | Pd | 0.65 |
| Zn | 0.93 | Ir | 0.48 |
| Pb | 0.94 | Pt | 0.86 |
| Ni | 0.57 | Mn | 0.92 |

The effect of overvoltage may be enough to cause the deposition of some metal from its ions in a solution under conditions where hydrogen evolution would be expected. The phenomenon of overvoltage is not completely understood and there are several theories which attempt to explain its occurrence; the resistance of a layer of hydrogen surrounding the electrode, the difficulty of bubble formation, and the condition of the metal in the electrode, have all come in for attention.

Suppose that a molal solution of $NaNO_3$ is to be electrolyzed between platinum electrodes with the use of a small current and a voltage not greatly in excess of that necessary to start electrolysis. Any aqueous solution at ordinary temperatures contains some $H^+$ ions and some $OH^-$ ions, even though it be strongly acid or basic. The product of the concentration of $H^+$ and $OH^-$ ions must always equal $1 \times 10^{-14}$ at ordinary temperatures. Increasing the concentration of one ion necessarily decreases that of the other but it will never be entirely absent. We have present, therefore, positive $Na^+$ ions and negative $NO_3^-$ ions in fairly large concentrations. The activity of these ions will be in the neighborhood of 0.7. There will also be some $H^+$ and $OH^-$ ions in very low concentration. All four ions aid in carrying the current through the solution, but when the cathode is reached, either the $Na^+$ ions must be discharged to give Na metal or $H^+$ ions to give hydrogen gas, the addition of an electron to each ion being necessary. Which of these will be liberated is determined by the potential of the ions toward the electrode and their concentration according to the formula

$$E = E_0 - \frac{0.05915}{N} \log \frac{1}{a'}.$$

Since the process occurs in the order $Na^+$, Na the sign for the potential must be changed, giving −2.7125, and, although there is no sodium on the electrode, if sodium were deposited it would act as an electrode of sodium. $E_{Na^+Na^0} = -2.7125 - \frac{0.05915}{1} \log \frac{1}{0.7}$, $E = -2.7125 - 0.05915 \times (-0.155) = -2.7125 + 0.0092 = -2.7$ volts. This means that the discharge of $Na^+$ ions to yield sodium metal would require the application of about 2.7 volts. Now for the $H^+$ ion whose concentration is $1 \times 10^{-7}$, the expression $\log \frac{1}{10^{-7}}$ becomes $\log 10^7$ which equals 7.

$$E_{H^+,\,H_2} = 0 - 0.05915 \times 7 = -0.413 \text{ volt.}$$

In addition the overvoltage for hydrogen from smooth platinum must be considered and since this amounts to about 0.18 the potential needed to discharge hydrogen is about −0.593 volt, a negative voltage meaning the application of electricity. It is seen from this that the discharge of $Na^+$ ion would require the expenditure of more energy than that of the $H^+$ ion. According to the principle of Le Chatelier, then, $H_2$ gas will be liberated and $Na^+$ ions will remain unchanged in the solution. A great increase in the concentration of the $Na^+$ ion, or polarization due to the use of too high voltage, might result in the deposition of some sodium by al-

[4] TAYLOR, H. S., *loc. cit.*, p. 840.
[5] TAYLOR, H. S., *loc. cit.*, p. 844.
[6] TAYLOR, H. S., *loc. cit.*, p. 849.

lowing the hydrogen potential to exceed that for sodium or to be in the same range so that they might be discharged simultaneously.

Similarly the $OH^-$ and $NO_3^-$ ions are attracted to the anode and the one of these to be discharged again depends on the potential required. The $OH^-$ ion, if discharged, decomposes into water and oxygen gas, while $NO_3^-$ ions probably require a very high potential to discharge and are not discharged at all under these conditions. Glasstone[7] estimates the discharge potential of $SO_4^{--}$ at about 2 volts, and that of $NO_3^-$ would doubtless be about the same. The $OH^-$ ion will discharge at the voltage required by the formula: $E = E_0 \ldots$, etc. $E_0$ here for $OH^-$, $O_2$ from the table is $-0.3976$, and since the activity of the $OH^-$ ion will be the same as that of the $H^+$ ion the expression becomes $E_{OH^-,O_2} = -0.3976 - 0.413 = -0.81$. To this must be added the oxygen overvoltage for platinum ($-0.86$), yielding a total voltage of $-1.77$, interpreted as meaning that 1.77 volts must be applied to cause the discharge of oxygen gas under these conditions. This is in agreement with the general statement that the decomposition potential for a salt yielding hydrogen and oxygen during electrolysis is about 1.7 volts.

It will be seen that this explanation is much simpler and more in keeping with modern knowledge than the secondary action theory still often used. According to this interpretation, the "primary products" are said to be sodium metal at the cathode from the $Na^+$ ion and a hypothetical $NO_3$ from the $NO_3^-$ ion at the anode. The sodium, being formed in the water, at once reacts with it to form NaOH and hydrogen gas. In like manner the $NO_3$ is supposed to react with water which surrounds it to form oxygen gas and $HNO_3$. These latter products are thought of as "secondary products." The NaOH is then said to neutralize the $HNO_3$, forming $NaNO_3$. It is explained that the $H^+$ ion parts with its charge more easily than the $Na^+$ ion, and hence the metallic sodium must react with the water to form hydrogen gas and the $Na^+$ ion. If it is true that the $H^+$ ion is more easily discharged than the $Na^+$ ion then it will be discharged at first at the cathode as hydrogen gas and the sodium ion will undergo no change. It may be objected that the anode region does become acid and the cathode region basic, proving that NaOH and $HNO_3$ are formed. Acidity is caused not by formation of an acid molecule, but by an excess of $H^+$ ions, or by a depletion of $OH^-$ ions, and since the latter are being depleted around the anode the $H^+$ ions will be in excess. A similar argument holds for the basicity of the cathode region.

The electrolysis of a molal solution of cupric sulfate between inert electrodes would yield at the cathode a choice between the discharge of copper metal or of hydrogen gas, since the water furnishes $H^+$ and $OH^-$ ions. From the voltage equation ($E_{0Cu^{++},Cu} = +0.3448$, and activity about 0.5), $E_{Cu^{++},Cu}$ is found to be about $+0.33$ volt while the liberation of hydrogen gas from such a solution requires a potential of $-0.593$ volt, showing that the deposition of copper is spontaneous, while the evolution of hydrogen requires the application of electricity. As the copper is deposited, the $Cu^{++}$ ions will be depleted and the relative concentration of $H^+$ ions increased until, if no additional $Cu^{++}$ ions are added, hydrogen gas may be evolved or simultaneous liberation of hydrogen and copper may occur.

At the anode, the choice is between the discharge of $OH^-$ and $SO_4^{--}$ ions. From previous considerations, it is seen that the discharge of $OH^-$ ions even from practically neutral solutions requires the application of much less voltage than for an anion of the nitrate, sulfate, or phosphate type. Oxygen gas will then be liberated and the $SO_4^{--}$ ion will remain in solution. The discharge of $OH^-$ ions will lead to an increase in $H^+$ ions and so to an increased acidity.

If copper electrodes are used in place of platinum, the cathode reaction is unchanged except that it is still more difficult for hydrogen to be discharged from copper electrodes than from platinum. At the anode, however, a new reaction is possible; the copper electrode may dissolve to form $Cu^{++}$ ions. This requires the application of about 0.35 volt, while discharge of $OH^-$ ions requires about 1.7 volts, and discharge of $SO_4^{--}$ ions still more. The anode reaction then consists of the solution of the copper electrode to form $Cu^{++}$, the principle of which is used in the purification of copper, since the ions formed deposit on the cathode in the pure form and the anode may be of crude copper.

Other examples which are of interest may be included here. The electrolysis of hydrochloric acid of moderate concentration results in the formation mostly of chlorine gas; in more dilute solutions such as below $M/32$ it is said to result in the liberation of oxygen gas. As a matter of fact, recent work[8] has shown that actually a mixture of oxygen and chlorine is obtained varying with the relative concentrations of $Cl^-$ and $OH^-$ ions.

Similarly, the electrolysis of a moderately concentrated solution of KCl will yield hydrogen gas at the cathode and chlorine gas at the anode mixed with a little oxygen gas, while a more dilute solution will yield less chlorine and more oxygen gas.

It is seen from these remarks that all phenomena formerly explained by the "secondary action" theory are quite satisfactorily explained by saying that the final products are those actually formed by electrolysis and there is no need to resort to the concept of "secondary products." In all fairness, however, it should be said that there may be true secondary products in some cases, for example, the formation of hypochlorites and chlorates under some conditions when sodium chloride solution is electrolyzed, although again it may turn out that the hypochlorite is the real primary product instead of chlorine.

[7] GLASSTONE, S., "The electrolysis of aqueous solutions," *Sch. Sci. Rev.*, **16**, 335 (Mar., 1935). This entire article, pp. 328–41, is by a recognized British authority on electrochemistry, and is highly recommended for study.

[8] TAYLOR, H. S., *loc. cit.*, pp. 340–1.

# CRYSTAL CHEMISTRY

## *III. THE STRUCTURE OF BINARY COMPOUNDS. THE AX COMPOUNDS*

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THE common structures of the AX compounds are shown in Figure 3. Of these, the NaCl structure occurs most frequently, perhaps because it tolerates a wider variation in the nature of its building stones than do the other types. To establish the conditions which favor this structure, we shall study the transition from this type to other typical AX lattices.

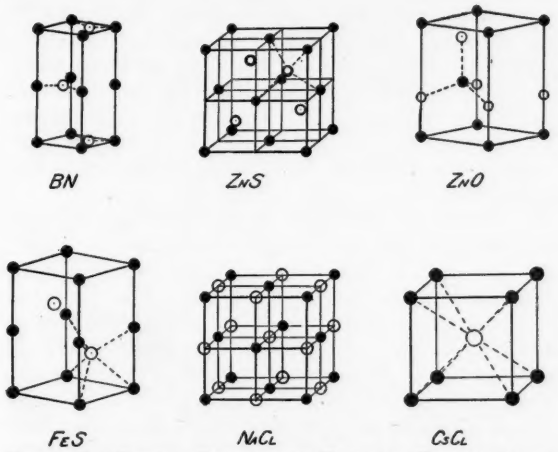


FIGURE 3.—TYPICAL CRYSTALLINE FORMS OF COMPOUNDS OF TYPE AX

The NaCl structure is typically ionic; its ions are relatively free from polarization effects and it is favored when the $R_A:R_X$ ratio is greater than 0.41. It will become evident, presently, that this structure is not unequivocally dependent upon either a definite $R_A:R_X$ ratio or upon the existence of an ionic bond. To be sure, the NaCl structure prevails among compounds of positive and negative ions having the rare-gas configuration, those which would be expected to form the least distorted ionic bonds; but it does not follow that all crystals with the NaCl structure are ionic. One need only examine the data in Table 12 to observe that the occurrence of the NaCl structure does not depend entirely upon the radius ratio. If one proceeds on the assumptions (1) that the NaCl structure is favored when the $R_A:R_X$ ratio lies between 0.41–0.73, (2) that above 0.73 the CsCl structure is favored, while (3) below 0.41 the ZnS (ZnO) structure usually occurs (*1a*), there are many exceptions to be found in the table. A discussion of the data in Table 12, therefore, leads to a rather detailed study of the transitions: NaCl structure to CsCl structure; and NaCl structure to ZnS (ZnO) structure.

TABLE 12

THE STRUCTURES AND $R_A:R_X$ RATIOS OF SOME AX COMPOUNDS (Å.)

| *Cation* $R_A$ | | Li 0.68 | Na 0.98 | K 1.33 | Rb 1.48 | $NH_4$ 1.50 | Cs 1.67 | Tl† 1.50 | |
|---|---|---|---|---|---|---|---|---|---|
| *Anion* | $R_X$ | | | | | | | | |
| F | 1.33 | NaCl | NaCl | NaCl | NaCl | ZnO | NaCl | | Structure |
| | | 0.51 | 0.73 | 1.00 | 1.11 | 1.13 | 1.25 | | $R_A:R_X$ |
| Cl | 1.81 | NaCl | NaCl | NaCl | NaCl* | CsCl† | CaCl | CaCl | Structure |
| | | 0.37 | 0.54 | 0.74 | 0.82 | 0.83 | 0.92 | 0.83 | $R_A:R_X$ |
| Br | 1.96 | NaCl | NaCl | NaCl | NaCl* | CsCl† | CsCl | CsCl | Structure |
| | | 0.35 | 0.50 | 0.68 | 0.75 | 0.76 | 0.85 | 0.76 | $R_A:R_X$ |
| I | 2.19 | NaCl | NaCl | NaCl | NaCl* | CsCl† | CsCl | CsCl | Structure |
| | | 0.31 | 0.45 | 0.61 | 0.68 | 0.69 | 0.77 | 0.69 | $R_A:R_X$ |

* At high pressure these have the CsCl structure.
† At high temperature these have the NaCl structure.

| *Cation* $R_A$ | | Mg 0.71 | Ca 0.98 | Sr 1.15 | Ba 1.37 | |
|---|---|---|---|---|---|---|
| *Anion* | Rx | | | | | |
| O | 1.33 | NaCl | NaCl | NaCl | NaCl | Structure |
| | | 0.58 | 0.74 | 0.86 | 1.00 | $R_A:R_X$ |
| S | 1.74 | NaCl | NaCl | NaCl | NaCl | Structure |
| | | 0.41 | 0.56 | 0.66 | 0.75 | $R_A:R_X$ |
| Se | 1.96 | NaCl | NaCl | NaCl | NaCl | Structure |
| | | 0.37 | 0.50 | 0.59 | 0.67 | $R_A:R_X$ |
| Te | 2.18 | ZnO | NaCl | NaCl | NaCl | Structure |
| | | 0.33 | 0.45 | 0.53 | 0.60 | $R_A:R_X$ |

### THE TRANSITION NaCl STRUCTURE TO CsCl STRUCTURE

The occurrence of the CsCl structure seems, at first sight, to bear little relation to the radius ratio 0.73. Of the compounds listed in Table 12, there are sixteen for which the radius ratio is above 0.73 and only seven crystallize with the CsCl structure. This structure is favored for two compounds in which the radius ratio is too low. It appears that the CsCl structure is not a particularly stable arrangement of ions. The coulomb energy of the CsCl arrangement is greater than the energy for either the NaCl or ZnS structure: that is, the first is a less stable structure (*44*). The suggestion has been made (*45*) that the NaCl and ZnS structures are common because in them like atoms or ions are on a face-centered cubic lattice, each having a coördination number of twelve in reference to like neighbors. This is true of the large ions, the "lattice supporters" (Gitterträger) of Laves. In the CsCl structure, however, the coördination of the lattice supporters is only six, so that at the outset special circumstances must be expected to stabilize this structure. The conditions necessary to establish the CsCl structure have been discussed by Pauling in connection with the polymorphism of the rubidium halides (*46*). He concludes that this structure is stable for alkali halides with high anion deformability and large radius ratio. The rubidium, ammonium, and thallous halides, all with cations of comparable size, offer an opportunity to study the ef-

fect of polarization, independent of variations in radius ratio. Pauling's conclusions account satisfactorily for the structure of the rubidium and cesium salts; the radius ratio is the predominant factor here. The rubidium salts are obviously on the borderline in regard to radius-ratio and polarization properties and their polymorphism is quite natural. It is also evident that, in spite of their high radius ratios, no fluorides could be expected with the CsCl structure because the fluoride ion cannot be polarized appreciably. Furthermore, of KBr and RbI, both with the same radius ratio, only the latter has the CsCl structure because of the greater polarizability of the iodide ion.

A slightly different emphasis is placed upon the question by Goldschmidt (*47*), who proposes that the CsCl structure is favored when (1) the radius ratio is above 0.73, (2) the polarizabilities of anion and cation are not very different. Pauling shows why the large cations (Goldschmidt's polarizable cations) favor the CsCl structure. The ammonium halides fit this picture inasmuch as the ammonium ion is easily polarized. The predominance of the CsCl structure among intermetallic compounds (the beta phases) also appears to be consistent with Goldschmidt's views. The polarizability of the thallous ion, as calculated by Mayer (*48*), suggests that its polarizing power is probably comparable to those of rubidium and cesium, and the CsCl structure for the thallous halides is to be expected. Furthermore, it is true that no divalent AX compounds crystallize in the CsCl lattice, and the polarizabilities of divalent cations and anions differ more than those of univalent cations and anions. As the valences of both ions increase, the polarizing influence of the cation increases more, proportionally, than the polarizability of the anion.

In brief, the CsCl structure is not particularly stable, but may be formed by univalent ions when the radius ratio is above 0.73.

### THE TRANSITION NaCl STRUCTURE → ZnS(ZnO) STRUCTURE

The ZnS structure may occur as the result of: (1) a decrease in $R_A:R_X$ ratio below 0.41; (2) the introduction of a strongly polarizing cation and an easily polarized anion; and (3) the occurrence of a covalent bond.

In the light of the foregoing discussion the interdependence of these qualifications becomes apparent. The bond is very likely to be partly covalent; when it is covalent it has strong directional properties (tetrahedral for the atoms which form the ZnS structure) which probably exert some influence upon the tetrahedral arrangement of the atoms in the crystal. Generally the properties of compounds with the ZnS-(ZnO) structure suggest that the bond is of an intermediate nature. The $R_A:R_X$ ratio need not be within the limits prescribed for the ZnS structure, since it is a secondary influence. Occasionally, the ZnS structure is found for compounds in which little or no polarization is to be expected. In such cases, the stability of the structure conforms closely to the $R_A:R_X$ limits (0.41–0.22) and this is the determining factor in its formation; the bonds are essentially ionic. As a general thing, however, the ionic bond does not predominate in the ZnS lattice.

Consider, with the above generalizations in mind, Table 12 and Figure 1 (first instalment). It may be said that the beryllium salts and MgTe, in Table 12, are largely ionic in spite of their structure; and that $NH_4F$ crystallizes in the ZnO structure, in spite of the $R_A:R_X$ ratio, because of the unsymmetrical ammonium ion. Indeed, it has been shown (*49*) that in crystalline $NH_4F$ one of the hydrogen atoms is drawn toward the fluoride ion. Possibly a hydrogen bond ties the fluoride to the rest of the molecule (*50*).

It is evident that the stronghold of the ZnS(ZnO) structure is among the AX compounds of the B-cations, the strongly polarizing cations $Cu^+$, $Ag^+$, $Zn^{++}$, $Cd^{++}$, $Hg^{++}$, $Ga^{+3}$, $In^{+3}$. That the covalent bond prevails in most of these is indicated by the constancy of the interatomic distances in each series, as shown in Table 11A. This same criterion may be used to select from Table 11A those compounds which are not strictly covalent. These are AgI, MgTe, BeO, and probably AlAs and AlSb.

The relation between ionic sizes and the NaCl and ZnS structures may be viewed from another angle. The X atoms or ions of both these AX structures are on a face-centered cubic lattice. When the metal is relatively large, it occupies the largest interstices in this lattice, those in the centers of octahedra, with six neighbors, and the simple cubic, NaCl lattice is formed. When the metal ions are much smaller they occupy the alternate second largest interstices in the face-centered cubic lattice, those in the centers of tetrahedra, and the ZnS lattice is formed.

Instead of correlating changes in structure with $R_A:R_X$ ratios, Niggli (*51*) uses limiting ratios for interionic distances from a central ion or atom to the first and second "coördination spheres." Thus, an atom A in a NaCl lattice has six neighbors X in the first coördination sphere and twelve neighbors A in the second sphere. This lattice is stable when the ratio of the distance A-X to A-A is $1:1.414 = 1:\sqrt{6/3}$. In the ZnS structure each atom A has four neighbors in the first sphere and twelve in the second, and the structure is stable when $A\text{-}X/A\text{-}A = 1:1.636 = 1:\sqrt{8/3}$. For the CsCl structure the ratio is $1:1.153 = 1:\sqrt{4/3}$.

### THE TRANSITION NaCl STRUCTURE → ZnO STRUCTURE → ZnS STRUCTURE

The ZnS and the ZnO structures are both characterized by the coördination number four; in both, the arrangement is tetrahedral. The X atoms or ions are on a face-centered cubic lattice in ZnS, and on a hexagonal, close-packed lattice in ZnO. All that has been said of polarization and bond type applies to the ZnO structure as well as to the ZnS structure.

From crystal structure data, however, it is quite

evident that the ZnO structure represents an intermediate step in the transition, NaCl structure to ZnS structure. The data in Table 13 show this very clearly.

TABLE 13

THE TRANSITION, NaCl to ZnO to ZnS

| | O | S | Se | Te |
|---|---|---|---|---|
| Cd | NaCl | ZnO<br>ZnS | ZnO<br>ZnS | ZnS |
| Zn | ZnO | ZnO<br>ZnS | ZnS | ZnS |

| *Compound* | *Structure* | *Compound* | *Structure* |
|---|---|---|---|
| NaF | NaCl | NaI | NaCl |
| MgO | NaCl | MgTe | ZnO |
| AlN | ZnO | AlSb | ZnS |
| SiC | ZnS | | |

Evidently, as polarization increases, the trend is NaCl → ZnO → ZnS, but the conditions for the formation of these last two structures are so nearly alike that many compounds are found to crystallize in either form, depending upon the temperature or other conditions.

### THE TRANSITION NaCl STRUCTURE → NiAs STRUCTURE

The nickel arsenide structure, found in zone VII in Figure 1, is peculiar to compounds of the transition elements (Cr, Mn, Fe, Co, Ni, Pd, Pt) with S, Se, Te, As, Sb, Bi. The properties of crystals of this group are distinctive. As in the wurtzite structure, the anions—"lattice supporters"—are on an hexagonal close-packed lattice. The metal atoms occupy positions at the centers of slightly distorted octahedra, on a simple hexagonal lattice, giving the crystal a coördination number of six. Each anion, X, is at the center of a trigonal prism and has six nearest neighbors. The arrangement of the metal atoms is suggestive of chains running in the direction of the *c* axis.

The attempt has been made (*52*, *53*) to correlate the transition NaCl → NiAs with a limiting value of the radius ratios. As might be expected, since there is no change in coördination number involved in this transition, the radius ratio values for the two structures are very much alike. In fact, these are not ionic crystals, but are built of atoms, and there is little point in analyzing them in terms of ionic radii. Crystal structure data which illustrate the transition from the NaCl to the NiAs structure are tabulated in Table 14.

Polarization increases from the upper left- to the lower right-hand corner of the table and is an important factor in the stabilization of the NiAs structure. Inasmuch as the transition elements are known to be more strongly polarizing than the A-cations, but less polarizing than the B-cations, it might be supposed that the NiAs structure is the result of an intermediate degree of polarization. Were this the case, however, one would expect to find the NiAs structure between the NaCl and ZnO structures in the series of cadmium or zinc compounds, attached to Table 14 for comparison. Without question, the influence of the electronic structure of the transition elements—the incomplete eighteen-electron shell—is primarily responsible for the NiAs structure.

Within the group there are some interesting systematic structural changes caused by polarization properties and variations in atomic radii. Consider the variations in the axial ratios, as listed in Table 14 (*54*).

TABLE 14

THE OCCURRENCE OF THE NiAs STRUCTURE

| | *Atomic Radii* | *Ionic Radii* | O | S | Se | Te | As | Sb | |
|---|---|---|---|---|---|---|---|---|---|
| Mg | 1.60 | 0.78 | NaCl | NaCl | NaCl | ZnS | | | Structure |
| Ca | 1.97 | 0.98 | NaCl | NaCl | NaCl | NaCl | | | Crystal Structure |
| Cr | 1.25 | | | NiAs | NiAs | NiAs | | NiAs | Structure |
| | | | | 1.65 | 1.62 | 1.56 | | 1.33 | Axial Ratio |
| Mn | 1.18 | 0.91 | NaCl | NaCl | NaCl | NiAs | NiAs | NiAs | Structure |
| | | | | | | 1.62 | 1.54 | 1.40 | Axial Ratio |
| Fe | 1.27 | 0.83 | NaCl | NiAs | NiAs | NiAs | | NiAs | Structure |
| | | | | 1.69 | 1.63 | 1.49 | | 1.26 | Axial Ratio |
| Co | 1.25 | 0.82 | NaCl | NiAs | NiAs | NiAs | | NiAs | Structure |
| | | | | 1.53 | 1.47 | 1.38 | | 1.34 | Axial Ratio |
| Ni | 1.24 | 0.78 | NaCl | NiAs | NiAs | NiAs | NiAs | NiAs | Structure |
| | | | | 1.55 | 1.46 | 1.36 | 1.39 | 1.30 | Axial Ratio |
| Pd | 1.37 | | | | | NiAs | | NiAs | Structure |
| | | | | | | 1.37 | | 1.37 | Axial Ratio |
| Cd | 1.49 | 0.98 | NaCl | ZnO | ZnS | ZnS | | | Structure |
| Zn | 1.32 | 0.83 | ZnO | ZnS | ZnS | ZnS | | | Crystal Structure |

In the NaCl lattice of the oxides, the oxygens are on a face-centered cubic (close-packed) lattice. It is therefore not surprising to find that, in the first compound of a transition series (*e. g.*, FeO, FeS, FeSe, FeTe) to crystallize in the NiAs structure, the axial ratio is somewhere near 1.63, the ratio for the ideal hexagonal close-packing of spheres. That is, there is a minimum of distortion of the lattice when the change from the cubic NaCl to the hexagonal NiAs occurs. The metal atoms, which occupied the centers of octahedra in the NaCl structure, are still found at the centers of distorted octahedra in the NiAs structure. With a given cation, as the anion is replaced by a more easily polarized anion, the axial ratio decreases; that is, the crystal is stretched more along the *a* axis than along the *c* axis. This means, in effect, that the metal atoms, which were distributed symmetrically throughout the lattice in the least distorted NiAs lattice, are moving farther apart in the direction of the *a* axis and are becoming more closely associated in the direction of the *c* axis; that is, the chain structure of the metal atoms is accentuated with increasing size and polarizability of the anion. Gradually, then, the metal atoms supplant the anions as the "lattice supporters." The question arises as to whether the bond is covalent and/or metallic in all NiAs structures, or whether it, too, changes gradually; being more nearly ionic, for example, in the undistorted CrS (axial ratio 1.65) and most covalent in the highly distorted CrSb (axial ratio 1.33). This cannot be answered with certainty, but the gradual transition is quite likely.

The NiAs group is of particular interest because, with respect to properties, it is intermediate between the intermetallic compounds of alloys and the covalent and ionic compounds. The most distinctive metallic properties of the group are opacity, electrical conductivity, and the ability of the lattice to dissolve an excess of one of the constituents—a process which is, of course, unusual in an ionic lattice.

The actual mechanism of solid solution for this structure has been studied, particularly for FeS and FeSe which may dissolve appreciable amounts of sulfur and selenium, respectively. The most significant feature of the solid solution is that, as the excess sulfur or selenium increases, the size of the unit cell, and particularly of the axial ratio, *decreases*. Thus:

| | *a* | *c* | *c/a* |
|---|---|---|---|
| FeS (1:1) | 3.43Å. | 5.79Å. | 1.69 |
| FeS (exc. S) | 3.43 | 5.68 | 1.66 |
| FeSe (1:1) | 3.61 | 5.87 | 1.62 |
| FeSe (exc. Se) | 3.51 | 5.55 | 1.58 |

These data lead to two conclusions. First, the metal chains are separated still farther by the excess metalloid (witness the decreased axial ratio). Secondly, the greater proportion of sulfur or selenium does not result, structurally, from the addition of an excess of the metalloid, but from the loss of some of the iron atoms. Some lattice points in the iron chains are missing. Such a structure is similar to the subtraction compounds, to be described in a later instalment.

### MISCELLANEOUS AX CRYSTALS

The crystal chemistry of the CsCl, NaCl, NiAs, ZnO, and ZnS structures has been discussed in some detail. There are a few other AX crystals of considerable interest.

*Boron Nitride, BN.* Boron nitride is isomorphous with graphite. It is a net lattice, and the only example of an AX compound crystallizing with a coördination number of three. Graphite and boron nitride offer another illustration of the rule found for so many ZnS structures; that there is a similarity of structure in a series of compounds in which A stands as many places before a fourth group element as X stands after the same element. In BN and graphite, as might be anticipated, not only the structures, but also the interatomic distances are the same.

*The Mercurous Halides* are, in a sense, molecular lattices which lend definite support to the validity of the formulas as they are usually written, *i. e.*, $Hg_2Cl_2$, $Hg_2Br_2$, and $Hg_2I_2$. They may also be looked upon as distorted NaCl lattices.

*Molecular Lattices.* Calculations of the stabilities of the different ionic lattices, based on lattice energies, have shown that, as the polarizability ($\alpha$) increases and the radius of the cation ($r$) decreases, the resulting lattice energies favor the stability of a molecular rather than an ionic lattice (*55*). This is shown in Figure 4, where it is evident that for values of $\alpha/r^3$ greater than *ca.* 0.4, the molecular lattice is more stable. Only $H^+$, carbon, and nitrogen are small enough to form molecular lattices, and the hydrogen halides, carbon monoxide, and nitric oxide are the only AX compounds of this type.

### SUMMARY

In this section the first law of crystal chemistry has been applied to the study of the structure of AX compounds. The structure of a crystal is determined by the relative number, the relative sizes, and the polarization properties of its building stones. In order to reckon with polarization effects, it has been necessary to consider the various methods of measuring polarization and the several kinds of data from which polarization properties may be qualitatively estimated. The influence of polarization on the ionic and covalent bonds has been studied, and the outstanding characteristics of the ionic and covalent bonds have been discussed. It has been found that, while the ionic and covalent bonds each favor the formation of certain crystal lattices, they are not peculiar to these lattices.

The relation between relative sizes and polarization properties of AX compounds, as they have been developed, are summarized briefly in Table 15.

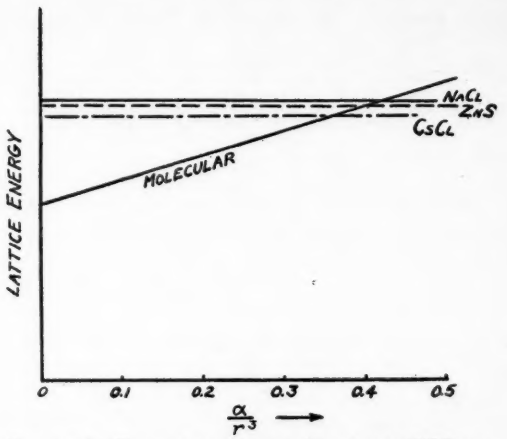


FIGURE 4.—RELATION OF LATTICE ENERGY OF AX TYPE CRYSTALS TO POLARIZABILITY ($\alpha$) AND CATION RADIUS ($r$)
From Born and Bollnow (*55*).

TABLE 15

| *Lattice Type* | $R_A$:$R_X$ | C.N.* | *Polarization* | *Prevalent Bond Type* | *Remarks* |
|---|---|---|---|---|---|
| CsCl | 0.73– | 8 | Minimum | Ionic | Univalent ions |
| NaCl | 0.41–0.73 | 6 | Negligible | Ionic (ex. ScN, TiC, PbS, PbSe, PbTe) | Uni- and divalent cations of rare-gas structure; and oxides and fluorides of other cations.† |
| NiAs | | 6 | Moderate to strong | Covalent-metallic | A = transition element; X, easily polarized. |
| ZnS-ZnO | 0.22–0.41 | 4 | Moderate to strong | Covalent | A = B-cation usually; if not, ionic bond predominates. |
| | | | | Polarized ionic; BeO, MgTe, BeS, BeTe, AgI | X = same as in NiAs. |
| BN (layer) | 0.15–0.22 | 3 | Strong | Covalent, metallic | |
| Molecular | | | Strong | Covalent, molecular | Intermol. forces, van der Waals; Intramol. forces, HF → HCl → HBr→HI; ionic → covalent. |

* C.N. = coördination number.
† The following are all, in a sense, distorted NaCl structures: PbO, SnO, PdO, HgO, GeS, SnS, HgS, $Hg_2Cl_2$, $Hg_2Br_2$, $Hg_2I_2$.

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# THE TECHNICAL REPORT

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NO FEATURE of scientific education has been so sadly neglected as the writing of a technical report. Research organizations of commercial companies, private institutions, and Government departments complain that chemists are notoriously bad writers, and many of them maintain "editorial departments" for the ostensible purpose of "editing" the reports of scientific work conducted by their chemists. In reality, the "editors" actually prepare the reports from the crudest sort of manuscripts which are little more than laboratory notes submitted as scientific reports. The chemist who can conduct a piece of research work and then write it up clearly and convincingly is such a *rara avis* that he usually rises rapidly to a commanding position in his research organization.

It is the purpose of this paper to describe a form of technical report which has been found suitable for a wide variety of research and development work with the hope that it may focus attention on this much-neglected part of a scientific education.

It will, of course, be conceded that a good course in English composition, with emphasis laid upon logical arrangement of ideas, is the first essential to the writing of a good report and the graduate chemist who has not had such a course lacks a very necessary tool of his profession. Such a course is indeed an essential not only to the writing of a good report but also to the proper planning of an economic research program.

A report has been aptly defined as an answer to a question.[1] This definition is particularly applicable to a scientific or technical report, and should be the guiding principle in the mind of every person entering upon the task of writing a technical report. When this is firmly grasped many of the terrors associated with report writing disappear. It follows that before starting upon the preparation of any report one must have very clearly in mind these two things:

1. What is the question which I am to answer?

2. What is the answer which I shall make to the question? The question or series of questions should be clearly stated in the introduction, the answer or series of answers, in the conclusion. What comes in between is designed to convince the reader that the answer to the question is the correct one. There are many ways of arranging this intermediate material, but for the sake of uniformity, that it may be easier to prepare, easier to read, and easier to understand, a standard arrangement is desirable.

The fundamental requirements of a good technical report are correctness, clearness, and completeness. Errors in grammar or punctuation are bad, but erroneous statements, erroneous calculations, or erroneous data constitute a serious indictment against the author.

A little careful thought and planning before the report is started will greatly facilitate the writing of the report and reduce subsequent revision to a minimum. It is very advisable to prepare an outline in as great detail as is feasible and have the outline approved by the immediate superior of the person writing the report or by the research director. The following is a skeleton outline which will explain in some detail the mechanical construction of a clear, logical, and convincing technical report.

I. *Introduction.*—This should be a brief and clear statement of the question to be answered, expressed in the form of the object of the work, and the authority for performing the work or the funds used in the work. Usually the first sentence should start as follows: "The object of the work described in this report was" .... This may be amplified by a sentence beginning: "The work was undertaken because".... The authority for the work may be the fulfilment of the requirements of a scholastic degree, a grant from a commercial or research organization, the direction of a board of governors or a research director, or in compliance with an authorized research program.

II. *Historical.*—This section is based upon a literature search which should be sufficiently thorough to assure against duplication of work. It should contain references to all previous work which is directly related to the problem, with brief statements showing the conclusions reached in the articles or reports referred to, in so far as they have a direct bearing on the problem in hand. Care should be taken that the facts cited from the literature have a direct bearing on the work to be described in the report. Scrupulous care should be exercised to give proper credit for previous work done, and comments on previous work should be so worded that there is no possibility of confusing these comments with those of the author being quoted. The form of reference used in *Chemical Abstracts* should be adopted.

[1] J. C. L. FISH, "Engineering economics," chapter XIX.

They may be inserted in the text in parentheses immediately following the sentence referring to the work quoted, they may be put at the bottom of the page as footnotes, or they may be collected in a bibliography at the end of the report, as seems most appropriate. References to original work should be used wherever possible rather than references to a previous summary.

III. *Theoretical.*—This section consists primarily of an analysis of the problem. By this is meant a discussion of the means chosen to solve the problem. Frequently it is necessary to split up the problem into two or more simple problems which may be solved separately. This section should usually be brief and should always be relevant to the problem under investigation. Many authors need to be cautioned against including rambling and irrelevant discussions remotely related to the theory involved.

IV. *Experimental.*—This section should contain a description of materials and apparatus used, procedures adopted, and data obtained. Data should be tabulated wherever possible and given a logical rather than a chronological arrangement. The section should be subdivided in a suitable manner indicating the subdivisions by some standard method of designation such as, for example, A, 1, a, (1), (a), in the order named. When the suggested designation is used, if IV is subdivided, the main subdivisions should be designated A, B, C, etc. If A is subdivided, the main divisions will be 1, 2, 3, etc. Careful study should be given to the subdivision of Section IV, since a proper presentation of the experimental work contributes very greatly to the clarity and force of the whole report. The subdivisions selected here, as in the entire report, should conform to any arbitrary style regulations imposed by the organization for which the report is being prepared. It is valuable to draw up a complete outline of this section before starting to write it. The notebook style should be avoided.

Discussion of the experimental data can sometimes be profitably included in the experimental section, following the experimental data to which it refers. This is particularly true if the experimental data have been logically classified and presented. In some reports, however, it is desirable to discuss the data as a whole in order to show how each phase of the experimental work contributes to the conclusions to be drawn, and in this case an additional main division of the report should be inserted directly after the experimental section and numbered V. Such questions as the degree of accuracy, the difficulties encountered, proposed remedies of difficulties, etc., can also be profitably discussed in such a section.

In order to make one's report complete in the broadest sense, it is, of course, necessary that the investigation be complete. This is not always within the control of the author. However, it is within his power to report all the data obtained (whether they support his conclusions or not) and to give an accurate description of the apparatus, materials, and procedure that will enable a future investigator to duplicate the work if necessary. Data should not be discarded merely because they are not concordant. Conflicting data may indicate the difficulties involved in the investigation or they may really indicate that the conclusions drawn are not justified. Scrupulous honesty is a necessary attribute of a successful chemist. He must not mislead anyone—not even himself.

V. *Conclusions.*—This should consist of concise clear statements of the answers to the questions implied in the introduction. If the conclusions are not clear-cut and unequivocal, the degree of their probability of correctness should be clearly stated. This section should not contain any of the discussion of the experimental data nor any statements not directly deducible from the data, nor should it include any conclusions drawn from other sources.

VI. *Recommendations.*—This section is required only in the case of reports which are submitted to an employer or a superior officer in an organization, and should consist of a recommendation as to the application to be made of the conclusions in the preceding section. The meat of the entire report is contained in the introduction, the conclusions, and the recommendations. The introduction states the question to be answered, the conclusion states the answer to the question, and the recommendation answers the question, "What shall we do about it?"

It is a mistake to clutter up the recommendation with a lot of advice as to what should be done if the work were to be repeated or carried farther. Such advice usually relates to procedures and methods and is thus addressed to succeeding laboratory workers and not to the employer. A place should be made for it in the section on discussion.

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There are many books available for those who wish to make a more extended study of technical report writing. The following brief list, while by no means complete, will be found useful.


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# *The* TRAINING *of a* RUSSIAN CHEMICAL ENGINEER*

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PUBLIC education in Russia is still in the evolutionary stage; with regard to curriculum it has, as yet, taken no definite form. It often happens that in the same school-type will be found entirely heterogeneous courses of study. Some developments in the right direction, however, are worthy of mention.

Since 1932 compulsory education has become universal throughout the entire Soviet Union. The technical schools are recognized as the most important and the most advanced. The curricula are devoted to the development of specialists; that is, students there are given little general background, but instead receive intensive training in narrow fields of their choice. Instruction in the building of chemical apparatus, for example, is an entire and separate course in the schools of chemical technology. It must be stressed, however, that there are many schools which, because of a deficiency of well trained professors, slight or entirely neglect this branch of instruction. There was therefore, at one time, a strong demand in Russia for scientific men skilled in the construction of chemical apparatus and experienced as instructors.

What is the training given a Russian chemical engineer and how much of this training is devoted to the principle of construction of chemical apparatus? These two questions were the basis for the writer's personal visit to Russia and they, among other pertinent questions, will be answered shortly.

At six or seven Russian children become of school age and are required to enter an elementary school, which they attend for seven years. They then enrol in a technical school having many highly specialized departments. It is not possible for the student to receive there a course in general chemistry; he must enrol, for example, in the department of coke-chemistry. Upon completion of the elected course (four years) the student becomes eligible to pursue his studies further in one of the technical universities, which, as previously mentioned, have departmental faculties.

One of the best-known Russian universities is the Mendeléeff Institute of Chemistry and Technology in Moscow. The course of study here lasts four years and is divided into twelve trimesters. The Mendeléeff Institute has two main divisions—the Chemical-Technical and the Mechanical-Chemical departments. Each of these is subdivided into the following faculties: Coke and Benzol; Dyestuffs; Fats and Oils; Sugar; Milling; and Heavy Inorganic Materials. In the Chemical-Technical department, the students study chemical processes and theory; their colleagues of the Mechanical-Chemical department, however, study machinery and apparatus. It should be obvious that the curriculum in chemical apparatus construction accomplishes more than that in most American, German, and Austrian universities, because most of them offer no lecture-courses on the subject.

The writer spoke with students and professors of the various faculties at Mendeléeff Institute while observing the system there and believes it possible to say that graduates are as well versed in the practical relations of their narrow branch as in the theoretical. Considering the fact that Russia needs to produce as many engineers as possible in the shortest possible time, the narrow, intense training of these engineers is somewhat justified. However, the fact should not be overlooked that the Russian engineer is less informed concerning general chemical questions and the relations of chemistry and technology than are American, German, and Austrian engineers.

A student, enrolled under the Coke and Benzol faculty in the Chemical-Technical department of the Mendeléeff Institute, submitted a program of his courses for the writer's examination. The program indicated that the student would attend one trimester (the seventh) of lectures on construction of apparatus used in the coke and tar industry. In the lecture room and laboratory the machinery and apparatus necessary to this industry will be described, planned, and constructed. (In the Mechanical-Chemical division construction and production will be stressed.) Frequent excursions will be made to factories in order to observe common practice and to study the machinery and apparatus in operation.

Many of the university students are not graduates of the technical schools. These have spent much time in actual practice. A three-year preparation course is required of them before admittance to a university is granted.

Examinations are dispensed with in Russian universities, but assignments are not. The instructor evaluates the progress of his students by their recitations and discussions. Low-ranking students, however, must take examinations. If they are thus shown to be incapable of carrying on the work, the matter is taken up by the faculty and they are dropped from the university. The state and the industries contribute to

* Translated from the German by H. W. PEEL, JR.

† Consulting engineer.

Russian university students a reasonably high, monthly scholarship. A state regulation requires that 70% of all university students must be workers or children of workers and allows only 30% from all other classes.

In Russia today there are about 170,000 schools with more than 660,000 teachers and over 26 million pupils. (These figures may be compared with 106,000 schools, 250,000 teachers, and 8 million pupils for the year 1913–14.) There are also about 800 colleges and technical universities with an enrolment of about 550,000 students; more than 3500 technical schools with over 800,000 students; nearly 950 workers' faculties (extension courses for workers) with perhaps 370,000 students; and more than 3900 factory and shop apprentice schools with nearly 1 million students.

A complete list of Russian universities and technical universities is not available. Three of the outstanding ones, which have faculties for instruction in chemical apparatus building, are: Mendeléeff Institute, in Moscow; Uljanow Lenin University, in Kazan; and Institute Chimplast-Mace, in Leningrad (for research only, not instruction).

# PREMEDICAL TRAINING

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A FEW years ago, the student who expected to study medicine was advised to consult the catalog of the medical school he expected to enter and then plan his premedical course accordingly. Such advice is good if the student can be certain that he will be admitted to the school of his choice. Because most medical schools of today have a great many more applicants for admission than they can possibly accommodate, the person who wants to be reasonably sure of being accepted by some school sends in his application to several different medical schools. It therefore becomes necessary for the student so to plan his course that it will fulfil the requirements for admission to any school.

There are three sources of information available for the student who wants to know how to be well equipped for the study of medicine. He can study the catalogs of the medical schools. But he will find in many instances that the catalogs give the minimum requirements of the American Medical Association only.

He can go to persons within his college who give guidance on vocational subjects or to his own professors. Unless these persons have made a real study of the situation their information is not complete, and quite frequently includes considerable misinformation.

Finally, the prospective student may talk to physicians of his acquaintance and attempt to learn from them what courses are desirable. While it may be a valuable experience to talk to the physician, the student cannot hope to get much help in the selection of his studies. The individual physician has not had contact with many different medical schools, and, unless he has kept in touch with the changes in curricula, his advice will not meet the situation.

The deans of the medical schools are the only ones who have a broad vision based upon experience. They are the only ones who are in position to judge how the various medical students are aided or handicapped by the nature of their premedical training.

In 1930 an attempt was made to help the student in his preparation for the study of medicine. A questionnaire was sent to the deans of some of the Class A medical schools asking them to appraise various college courses as to their premedical value.

This partial information[1] was found to be so helpful that the authors believed it worth while to bring it up to date and to extend it by including reports and comments solicited from all the Class A medical schools of the country.

As in the earlier study a questionnaire was sent to the deans with the request that they designate what courses, (1) they require, (2) they recommend, (3) they are doubtful as to the value of, and (4) they do not desire. The following schools and universities replied: Alabama, Baylor, Boston, Chicago (Rush Medical), Cincinnati, Columbia, Cornell, Creighton (Nebraska), Detroit College of Medicine and Surgery, Emory, Georgetown, George Washington, Georgia, Hahnemann Medical College and Hospital of Philadelphia, Harvard, Illinois, Iowa, Johns Hopkins, Long Island College of Medicine, Louisville, Loyola, Maryland, Michigan, Minnesota, Mississippi, Missouri, Nebraska, Northwestern, Ohio State, Oregon, Pennsylvania, Pittsburgh, Tulane, Union (Albany Medical), Utah, Virginia, Yale, Washington, Western Reserve, Wisconsin, Women's Medical College of Pennsylvania. Summaries of the appraisals are given in Table 1.

Since it is important for the student to equip himself for the best possible work in medical school and in after life it is desirable that he give careful consideration to those courses which are either required or recom-

[1] GRADY, ROY I., "Chemistry in the college curriculum of the premedical student," J. CHEM. EDUC., 9, 111 (Jan., 1932).

TABLE 1

SUMMARY OF REPLIES

| Subject | Sem. hrs. | Requiring | Recommending | Doubtful | Not Desiring | Requiring or Recommending |
|---|---|---|---|---|---|---|
| Biology: | | | | | | |
| General | 4 | 34 | 2 | 1 | 1 | 36* |
| Zoölogy | 4 | 35 | 3 | 0 | 0 | 38* |
| Vertebrate Anatomy | 4 | 16 | 25 | 0 | 0 | 41* |
| Physiology | 4 | 1 | 8 | 15 | 14 | 9 |
| Vert. Embryology | 4 | 6 | 26 | 5 | 2 | 32* |
| Animal Histology | 4 | 0 | 12 | 11 | 13 | 12 |
| Histological Techn. | 4 | 0 | 9 | 17 | 10 | 9 |
| Genetics | 4 | 3 | 25 | 6 | 0 | 28* |
| Chemistry: | | | | | | |
| General Inorganic | 8 | 41 | 0 | 0 | 0 | 41* |
| Qualitative Anal. | 4 | 20 | 18 | 1 | 0 | 38* |
| Quantitative Anal. | 4 | 18 | 17 | 4 | 0 | 35* |
| Adv. Quant. Anal. | 4 | 0 | 11 | 16 | 1 | 11 |
| Organic, 1st sem. | 4 | 41 | 0 | 0 | 0 | 41* |
| Organic, 2nd sem. | 4 | 31 | 7 | 0 | 0 | 38* |
| Food and Nutrition | 3–6 | 0 | 8 | 16 | 7 | 8 |
| Physical | 4–8 | 1 | 37 | 3 | 0 | 38* |
| Biochemistry | 4 | 0 | 4 | 14 | 16 | 4 |
| Economics | 6 | 1 | 28 | 2 | 1 | 29* |
| English: | | | | | | |
| Freshman Literature | 6 | 35 | 5 | 0 | 0 | 40* |
| General Literature | 6 | 9 | 25 | 3 | 0 | 34* |
| French, Elementary | 10 | 23 | 11 | 3 | 1 | 34* |
| 2nd year | 8 | 11 | 13 | 4 | 1 | 24* |
| German, Elementary | 10 | 27 | 11 | 0 | 0 | 38* |
| 2nd year | 8 | 14 | 14 | 1 | 0 | 28* |
| Greek | 10 | 0 | 7 | 14 | 6 | 7 |
| History, European | 6 | 2 | 22 | 8 | 0 | 24* |
| American | 6 | 0 | 22 | 8 | 0 | 22* |
| Latin: | | | | | | |
| 2 yrs. High School | | 4 | 2 | 0 | 0 | 6 |
| 4 yrs. High School | | 2 | 21 | 4 | 0 | 23* |
| Cicero and Livy | 8 | 0 | 4 | 13 | 5 | 4 |
| Math., Trigonometry | 3 | 7 | 26 | 2 | 0 | 33* |
| Anal. Geometry | 3 | 1 | 17 | 8 | 1 | 18 |
| Philosophy | 3 | 1 | 22 | 6 | 1 | 23* |
| Physics | 8 | 41 | 0 | 0 | 0 | 41* |
| Adv. Physics | 4 | 0 | 14 | 11 | 2 | 14 |
| Psychology | 3 | 2 | 28 | 3 | 1 | 30* |
| Bible | 4 | 0 | 7 | 17 | 3 | 7 |
| Sociology | 3 | 1 | 28 | 4 | 0 | 29* |
| Speech | 3 | 0 | 23 | 5 | 1 | 23* |

* Required or recommended by a majority (twenty-two or more).

mended by the deans of the Class A medical schools. For this reason we have added another column in Table 1 indicating the total number of schools either requiring or recommending each subject. In this column those subjects which are required or recommended by a majority (twenty-two or more) of the schools are marked with an asterisk.

While the table clearly indicates the courses which are considered essential or desirable, the comments of the deans show that there is a flexibility which cannot be indicated in any table of data. In some schools there is a tendency to select a high-class candidate even though he may not have taken some of the courses which are highly recommended.

The dean of a mid-western school writes as follows:

"I think that we are all tending to much more generosity in subject matter of premedical curricula than seemed to be true a few years ago. I think we can say very definitely now that one of the major objectives of premedical education is to acquire a cultural background that will equip the medical man to hold his own in competition with other college graduates in all matters of general interest and culture."

The preparation in English is not entirely satisfactory. One dean writes:

"As professor of anatomy I have met the incoming students for the past twenty years, and the greatest criticism I have of the freshmen is their lack of knowledge of the English language and no appreciation of the roots from which the words have been formed. A dictionary apparently to the modern student is a book to be avoided."

Another states:

"The most uniform complaint I encounter from medical faculties is the inadequacy of students in handling English. I certainly think that six hours of English in a three-year program is hardly adequate."

Quite a number of the deans are expressing a decided preference for German instead of French where both cannot be taken. They prefer a usable knowledge of one or the other to a smattering of both. This trend toward the preference for German seems to be a development of the past six years.

Other comments by the deans, which should prove helpful, follow:

"I think the important thing is to provide in the premedical education a general preparation rather than specifically preprofessional."

Another writes:

"In general, it is not desired that courses be taken which anticipate courses to be given in the medical school, such as physiology and biochemistry. It is desired that students entering the medical school should have a good background of general education. This should not be limited to scientific courses, but should give the student a basis for advancing the knowledge not only of the chemistry of the body, but also of human beings as such."

Another:

"Subjects such as physiology, histology, embryology, biochemistry, etc., a part of the essential curriculum of medical schools, should not be taken in arts and science colleges because of the waste of time to the student. I mean to say, there are many other things that medical colleges do not teach that are sufficiently important that he cannot afford the time of duplications."

Another:

"Animal histology, histological technic, and genetics seem to me of somewhat doubtful value in the premedical work. A working knowledge of them is pretty apt to be gained in medical school and they therefore represent a duplication. It seems to me it would be much better to replace them with social sciences, politics and government, or history."

It should be kept in mind that it is impossible and undesirable to specify a standardized premedical course. The taking of numerous scientific and general courses in college will not necessarily insure success as a physician. Other factors such as those which derive from the qualities of the student, the teachers, context of courses, opportunities, and any others over which the student has no control have much to do with future success. In this connection the dean of an eastern medical school writes:

"I am convinced that there are several factors even more important than the courses taken. First of all, a medical student should be a man of character and ability and thoroughly enthusiastic about the practice of medicine. He should have a pleasing personality and be conscientiously interested in making the world better."

# TURNING ACCIDENTS *into* PROFIT THROUGH CAREFUL OBSERVATION

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THE June, 1933, number of THIS JOURNAL, page 379, carried a suggestion by the writer enlisting the help of teachers, students, and others to compile a list of: (1) discoveries or inventions made by accident; (2) examples to show the slowness of scientific progress; (3) incidents in which science has been too skeptical; and (4) discoveries that were made simultaneously and independently.

One might add a fifth topic: a list of substances that once were nuisances but now are valuable; for example, coal tar, gasoline, sawdust, chloramine T, bagasse, etc.; and a sixth topic, a list of substances for which a use should be found.

In connection with the fifth topic, it would be of interest and value to state the special turn of the chemical world or the turn of world affairs in general which caused the waste product to become of real worth.

The examples submitted to date with references and name and address of observer are offered for publication. The writer is anxious that more examples be sent in, because such lists, when more complete, could hardly fail to impress upon the student (1) the value of careful observations in experimental work and (2) the fact that scientific discoveries are "in the air" waiting for someone to pick them out.

Teachers looking for additional work for students who are ahead of their classes might use any one of the above ideas to good advantage.

## ACCIDENTAL DISCOVERIES

1. Laminated safety glass was accidentally discovered when Edouard Benedictus observed that a flask which had dropped from the top of a shelf to the floor, although badly cracked, still retained its original shape (*1*).

Mr. J. Wilson of the British Triplex Safety Glass Co., Ltd., King's Norton, Birmingham, England, gives, in the *Transactions of the Society of Glass Technology*, vol. 16, pp. 67–79, 1932, a summary from the original paper.

"One day (in 1903) he [Benedictus] was rearranging some flasks in the laboratory when he dropped one to the floor, a distance of 11 feet or so, but to his amazement he noticed that the flask, although cracked, remained intact—not a single fragment of glass had been detached. On further examination he found that the flask had originally contained a solution of nitrocellulose, but that the solvent had evaporated, leaving a strongly adherent inner film. He made a note on the label and thought no more about it.

"Sometime afterwards, however, he read an account of an accident to a young girl, who had been badly cut by glass in a motor accident. A few weeks later he read of a similar accident, and was sitting down after dinner thinking the matter over, when suddenly there appeared before his eyes an image of the broken flask. He leaped up, dashed to his laboratory, and concentrated on the practical possibilities of his idea. Next morning, dawn found him still there with the flask in his hands. For nine hours he had not stirred, but he had thought out a program which he proceeded to execute step by step. By evening he had produced, with the help of a letter-press, his first sheet of Triplex. In 1909, after six years of study, he took out his first French patent, and founded the Société du Verre Triplex."

2. The world's greatest nickel deposit in the Sudbury district, Ontario, was discovered accidentally when a surveyor noticed that at certain places his compass was deflected ten or more degrees from the normal (*2*).*

3. Experimenters sought an objective for eight years, then discovered something else: catalytic oxidation of coal-tar products (*3*).*

4. The self-lining alundum furnace is one more case of the achievement of an observant, technically trained man; an accidental observation (*4*).*

5. Gomberg expected hexaphenylethane but obtained triphenyl methyl (*5*).

6. Williamson, in attempting to prepare substituted alcohols, obtained a method of making ethers (*6*).

7. Helium was discovered in the atmosphere of the sun during a solar eclipse (*7*).*

Liquid oxygen was accidentally discovered when a French scientist opened the wrong valve but observed the moisture that settled. Blotting paper was accidentally discovered when someone tried to write upon some pulp that had been discarded from a paper mill, because a workman forgot to add sizing, and noticed it absorbed ink. Silver plating was accidentally invented when a scientist noticed that silver from a silver nitrate solution deposited on a wire carrying electricity which was used to decompose the solution. References are needed for these and many other accidental discoveries.

## SKEPTICAL RIDICULE

1. Bankers said to Bror Dahlberg, "Don't waste money on bagasse. Others have tried and failed." But Dahlberg could not be discouraged. The result was synthetic lumber, Celotex. This is an interesting story (*8*).*

2. When Napoleon offered a prize of a million francs for a practical process of extracting sugar from the beet, a cartoon appeared showing Napoleon in a nursery be-

* Items indicated by an asterisk were contributed by Greta Oppe, Ball High School, Galveston, Texas.

side the cradle of his son, squeezing a beet into his coffee, while the nurse has put a beet into the mouth of the baby saying, "Suck, dear, suck. Your father says it's sugar (*9*)."*

3. One of Frasch's acquaintances offered to eat all the sulfur that Frasch could ever pump out of the Louisiana salt dome. Frasch's own account of it is to be found in the reference (*10*).

4. When Mr. Newland read a paper on "The Law of Octaves" at a meeting of the London Chemical Society in 1866, Professor G. C. Foster said that any arrangement of the elements would present occasional coincidences, and inquired if Mr. Newland had ever examined an arrangement of the elements according to their initial letters. Twenty-one years later the Royal Society awarded Newland the Davy Medal for his discovery (*11*).

SIMULTANEOUS AND INDEPENDENT DISCOVERIES

1. Paul Kitaibel and Müller von Reichenstein discovered tellurium independently (*12*).*

2. Meissner of Halle and Karsten of Berlin, without any knowledge of Stromeyer, Roloff, and Berman's work, discovered cadmium (*13*).*

3. Dr. Boltwood of Yale discovered the parent substance of radium—ionium—which was discovered independently and simultaneously by Hahn and Marckwald in Germany (*14*).*

4. In 1895 Ramsay in England, and Cleve and Langlet in Sweden were independent discoverers of terrestrial helium (*15*).

5. Daniel Rutherford discovered nitrogen. Scheele, Priestley, and Cavendish each discovered it independently at about the same time (*16*).*

6. An unusual and interesting parallel occurs in the Hall-Heroult electrolytic process for the production of aluminum. Both these men were born in the same year, one in America and the other in France, in 1863, and both died in the same year, 1914. Both made their great invention simultaneously and independently at the age of twenty-three (*17*).

7. Illinium was discovered independently in 1926 by three sets of workers; by Hopkins, Harris, and Yntema in Illinois; by Cork, James, and Fogg in New Hampshire; and by Rolla and Fernandes in Italy (*18*).

8. Perkin in England, and Graebe and Liebermann in Germany patented nearly identical processes for the manufacture of alizarin, the first synthetic dye, only twenty-four hours apart (*19*).

9. Kossel in Germany and Lewis in California independently related valency and atomic number in polar and non-polar linkage in 1916 (*20*).

10. van't Hoff and Le Bel simultaneously and independently published similar explanations of the cause of optical activity of certain compounds (*21*).

11. Kolbe and Frankland discovered (or proposed) independently and at nearly the same time the tetravalency of the carbon atom (*22*).

12. Mendeléeff and Meyer quite independently and, so far as we can tell, quite ignorant of Newland's and Chancourtois' work obtained a far clearer vision of the law of octaves about 1869 (*23*).

13. Couper and Kekulé simultaneously formulated theories of chemical valence (*24*).

* * * * *

The author is grateful for the ideas already sent in. Some of the lists should grow considerably more. If any reader observes any idea or ideas that will fit into any of the six lists the writer will be very happy to receive them and will give due credit to the observer.

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# NOTES *on the* MOVEMENT *of* CRYSTALLINE IODINE *in* SILICA GEL

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THE phenomenon of precipitate formation in gels has received the attention of numerous investigators, few of whom agree as to the exact mechanism of such deposition. Any observation that may tend to clarify the problem is therefore of value. In the course of certain studies on crystal formation in gel media it was observed that crystalline iodine offered an excellent means for studying the mechanics of crystal formation, movement, and re-solution.

In general, any strong oxidizing agent will deposit crystalline iodine in silicic acid gel, the deposition being periodic in the cases where no simultaneous gas formation takes place, and especially so when the rate of diffusion is slow, as when a concurrent or secondary reaction product is also deposited. Such reagents as potassium dichromate or permanganate with sulfuric acid, and nitric acid alone, have been used to deposit excellent specimens of crystalline iodine in silica gel. It is interesting to note that in the case of nitric acid the deposition of iodine takes place on the outlines of the flattened gas bubbles which are simultaneously formed, resulting in a non-periodic structure. This non-periodicity follows as a result of the rapidity of the diffusion process, the inhomogeneity of the gel structure due to the distortion by gas bubbles, and the natural tendency of depositing materials to arrange themselves at any point of irregularity or tension (*1*).

Chlorine displaces iodine from potassium iodide very readily, yielding periodic stratification. Slight movement, *en masse*, results, however. Movement is accentuated by the presence of hydrochloric acid. The ideal deposition for the study of iodine crystal transfer in gel media results from a replacement reaction by bromine. The gel was made by mixing equal quantities of 1.06 density water-glass with *N* acetic acid, the gel being made *N*/10 with respect to potassium iodide before solidification.

Upon covering the above gel with bromine water, immediate crystal formation resulted. Further action produced rapidly growing rhombohedral masses of crystalline iodine possessing the general form of the lead ferrocyanide crystal masses described by Hatschek (*2, 3*); in this case, there is end-to-end fusion of single large rhombohedra of iodine.

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As pointed out by Taber (*4*), the particular shape of the deposited crystals and their subsequent growth will result from the operation, individually or concurrently, of at least three factors: the tendency to produce forms of a somewhat regular polyhedral character under the simultaneous action of the surface tension and the forces of molecular orientation, and the modification of growth in different directions by external forces.

Longitudinal growth of crystal masses was observed to take place along pre-determined planes. These force- or stress-planes were, in general, continuous with the faces of the end crystal, *i. e.*, at the growth zone, and manifested themselves as minute cracks sufficiently different from the medium in refractive index to be readily observable. These stress-planes were observed in single rhombohedra as well, growth invariably following the pattern pre-determined by them, their pattern, in turn, having been pre-determined by the shape of the original ultramicroscopic crystal.

After growth had resulted in crystals about a centimeter in length, the whole crystalline mass moved downward into the tube as a result of re-solution of the crystals in the excess of entering reagent. The diffusion front, as shown by the deep red color of the gel, always preceded the crystal front by a relatively large distance. Immediately below the crystal front, throughout the area containing the crystals, and for a short distance above the crystal band, the gel was stained a decided orange color. The remainder of the distance to the surface was light yellow.

The color scheme was interpreted on the basis of analysis of carefully sectioned areas as follows. Displacement of iodine from potassium iodide by bromine resulted in the formation of potassium bromide and free iodine. The latter formed the soluble reaction product $KI_3$, which diffused forward and backward. Moving backward, it met the higher concentration of bromine, forming KBr·IBr. This product also diffused in both directions. In its backward movement it encountered more bromine, thus freeing iodine which deposited at the crystal front.

At the rear of the crystal band, the bromine dissolved the precipitated iodine, forming KBr·IBr, which under the influence of the greater concentration of bromine in the rear moved forward, keeping a short distance behind the dissolving iodine crystals. The uppermost strata contained only potassium bromide and free bromine.

When diffusion of bromine was stopped three distinct mechanisms were apparent. The masses grew slightly by the deposition of iodine on the crystal front. Re-solution having been discontinued, the crystal band as a whole remained stationary and only single scattered crystals of iodine grew in the region below the band. After a time, the whole crystal band began to move backward, *i. e.*, up.

The phenomenon of backward diffusion of initial reaction product here noted is similar to that described by Lloyd and Moravek (*5*) for the periodic precipitation from the system potassium iodide–lead nitrate, the visible reaction product in their case being $KI \cdot PbI_2$.

A further example of diffusion was shown by the following experiment. A blank silica gel, *i. e.*, one containing no potassium iodide, was covered after solidification to a depth of about one centimeter with a silica gel $N/10$ with respect to potassium iodide. After gelation, the composite gel was covered with bromine water. The resultant crystal band moved through the interface with no apparent distortion or discontinuity in the individual crystals, and on down into the blank gel. The color scheme was identical with that already described.

The most interesting characteristic of the redissolving of the iodine crystals was the skeletal formation that invariably preceded the complete disappearance of the iodine. The outlines of the faces of the crystal, shown by a series of planes parallel to each face, were last to dissolve. Since these last traces of iodine followed so closely the crystal pattern, we must infer that when the crystal was formed, adsorption took place on the crystal faces as they were built up, perhaps on the stress-planes already noted, and that the rate of re-solution was appreciably diminished in these planes due to the protective action of the sorbed material. After complete disappearance of the crystal, its outline remained indelibly stamped into the gel, as portrayed by the difference in index of refraction of the volume previously occupied by the crystals and of the surrounding gel media.

The following conclusions derived from a consideration of these observations seem justifiable.

1. Deposition of crystalline iodine in silica gel may be periodic or non-periodic depending upon the rate of diffusion of entering reagent and the chemical nature of the reaction.
2. Crystallization does not result at the diffusion front but some distance in its rear.
3. An iodine crystal apparently exerts a pressure in a plane continuous with its faces, this pressure resulting in a visible stressing of the gel structure.
4. Movement of iodine crystals in silica gel appears to be the result of re-solution at the rear of the crystal mass and deposition at the crystal front. The moving crystal mass leaves an outlined path as a record of its passing.
5. It is the outline of the iodine crystal which dissolves last when re-solution takes place.

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# pH DETERMINATIONS *in* ELEMENTARY CHEMISTRY

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MOST college courses in elementary chemistry now include some discussion of the meaning of pH, and of its applications. However, because of the high prices of colorimetric standards, indicator dyes, and electrical apparatus, little laboratory work has been attempted in this field. Except for high cost, the colorimetric method is well suited to elementary work for the scheme is easily understood and a number of important principles can be illustrated with it.

The following simplified system, which is economical in regard to both time and money, has been used at Colgate for two years and has proved eminently satisfactory. Even though the pH determinations are merely approximate, the important principles are illustrated and the student is given first-hand experience.

The six indicator dyes listed below are used.

| | *pH Range* | *Color Range* |
|---|---|---|
| Methyl violet | 0–3 | yellow-violet |
| Methyl orange | 3–5 | red-yellow |
| *p*-Nitrophenol | 5–7 | colorless-yellow |
| Phenolphthalein | 8–10 | colorless-red |
| Alizarin yellow | 10–12 | yellow-blue |
| Indigo carmine | 12–14 | blue-yellow |

All of these dyes are rather common, most of them being available from an organic laboratory or purchasable at reasonable prices. All except phenolphthalein are water-soluble. Phenolphthalein is made up in alcoholic solution.

Solutions of the dyes are made up to such concentrations that two drops added to ten cubic centimeters of a solution of proper pH will give a moderately intense color. Since the same amount of dye solution (two drops) is added to both standard and unknown, it is not necessary to use accurately predetermined amounts of the dye. Alizarin yellow does not dissolve readily in water but will do so if a drop or two of sodium carbonate solution is added. This light buffering of the dye will not affect the pH determinations appreciably.

Standards are then made up which show only the two extremes of color for each indicator. For example, the two standards for methyl orange show only the red end having a pH of 3 or less and the yellow end having a pH of 5 or more. It is not necessary to use solutions of any exact pH value in making up the standards since the color of the dye undergoes no further change in solutions having pH values beyond the range of the particular dye. For example, the color of methyl orange is red in solutions of pH 1, 2, or 3, and yellow in solutions of pH 5 or more. Therefore, in making up the two standards for methyl orange, it is only necessary that one have a pH of 3 or less and the other, 5 or more.

However, the standards should have pH values not too far beyond those of the indicator limits; otherwise, some dyes tend to precipitate or to show another color range. Phenolphthalein, for instance, fades out in strongly alkaline solutions, while methyl violet tends to precipitate. The following solutions are suggested to show the proper color extremes of the respective indicators.

| | | |
|---|---|---|
| Methyl violet | pH 0 | Dilute sulfuric acid |
| | pH 3 | Aluminum chloride |
| Methyl orange | pH 3 | Dilute acetic acid |
| | pH 5 | Sodium chloride |
| *p*-Nitrophenol | pH 5 | Aluminum chloride |
| | pH 7 | Sodium bicarbonate |
| Phenolphthalein | pH 8 | Sodium chloride |
| | pH 10 | Sodium carbonate |
| Alizarin yellow | pH 10 | Sodium bicarbonate |
| | pH 12 | Sodium carbonate: a few drops of sodium hydroxide |
| Indigo carmine | pH 12 | Disodium phosphate |
| | pH 14 | Dilute sodium hydroxide |

It is well to make up a few hundred cubic centimeters of these solutions to keep on hand, for if the colored standards are exposed to light for any length of time, some of them fade considerably and must be renewed. Ten cubic centimeters of each solution is placed in a test-tube and two drops of the appropriate dye added. The tubes can then be stoppered and arranged in order of pH values, by pairs, against a white cardboard background. Names and pH values may be printed on the background.

In determining the pH of an unknown solution, the student starts by adding two drops of phenolphthalein to ten cubic centimeters of the unknown. If the solution remains colorless, the pH is 8 or less. He then adds two drops of *p*-nitrophenol directly to the unknown. If the color is yellow, the pH is 7–8; if pale yellow, 6–5; if colorless, 5 or less. If the solution is colorless, he adds methyl orange directly. If the color is yellow, the pH is 5; if an intermediate shade, 4; if red, 3 or less. If the pH is 3 or less, a fresh sample must be used and tested with methyl violet. If the solution is violet, the pH is 3; blue, 2; green, 1; yellow, 0. If the original unknown showed a red color with phenolphthalein, a fresh sample is used and tested with alizarin yellow. If the sample gives a blue color with alizarin yellow, a fresh sample must again be used and tested with indigo carmine. It is evident that, starting with no information concerning the pH of the unknown, not more than three different samples need be tested to determine the approximate value. Within the range 3–10, only one

sample is necessary if phenolphthalein is first used owing to the fact that both this dye and *p*-nitrophenol are colorless at their lower pH range.

In addition to its use for determining the pH of an unknown solution, the set can be used for studying hydrolysis of salts. If solutions of the following approximately normal salts are used, pH values ranging from 1 to 12 can be obtained: $NaHSO_4$, $AlCl_3$, $NaH_2PO_4$, NaCl, $NaHCO_3$, $Na_2HPO_4$, $Na_3PO_4$, $Na_2CO_3$. A comparison of the ionizations of equivalent solutions of strong and weak acids as well as of strong and weak bases can also be made. Thus, the pH of tenth-normal sulfuric acid is 1, while the pH of an equivalent solution of acetic acid is 3. Bray and Latimer[1] list a number of other interesting experiments involving the use of indicators.

The chief value of this set lies in its simplicity, low cost, and ease of upkeep. Standards are easily prepared and can be quickly renewed if they fade. No weighings are necessary in preparing either dye or standard solutions. Standards need not have exact pH values. In spite of its simplicity the system is not entirely fool proof as far as the student is concerned. Some students fail to realize, for example, that a solution which is red with phenolphthalein may have a pH considerably greater than 10, and make no further tests. One student who was consistently getting off colors was found to be adding the second indicator to a solution already colored by the first indicator. Another student was found trying to match a color between two different sets of standards. Of course, these are errors which would also be made using a standard colorimetric pH set and do not reflect on the particular method here described. They do indicate, however, the necessity of rather careful demonstration before turning the students loose.

[1] BRAY AND LATIMER, "A course in general chemistry," rev. ed., The Macmillan Co., New York City, 1932.

## EDMUND O. VON LIPPMANN*

ALL historians of chemistry are non-professional in the sense that none of them entirely derives his income from this discipline, but the purest amateur of them all is a successful technologist who, for many years, made a serious avocation of this labor of love. The title "Grand Old Man of Chemical Historians" undisputedly belongs to Edmund von Lippmann, who, born January 9, 1857, is now in his eightieth year, and whose current contributions give ample evidence that the vigor of his mind has not only remained unimpaired but actually increases as the years pass over his head.

The first stage of his serious education was received in his natal city, Vienna, where at the K. K. Akademische Gymnasium he was given a thorough grounding in the classics, an acquisition that has made possible many of his historical studies. His father, owner of a sugar factory and refinery, however, knew the advantages of a technical training, and after two years at the Gymnasium, the young man was enrolled in the Chemical Division of the Technical High School at Zürich. Here, for three years, he enjoyed the rare privilege of seeing in action two great scientists and teachers, Georg Lunge and Victor Meyer, and he carried with him to Heidelberg, where he took his doctorate under Bunsen in 1878, an indelible impression of what a school can do for its students.

von Lippmann, now ready to gain practical experience, spent the next two years in the sugar industry of Austro-Hungary, and did so well that he was called back to Germany to introduce the Steffen process of recovering sugar from molasses. He advanced rapidly in his profession, put into operation the new strontium process, and after directing several refineries was, in 1890, asked to head the refinery at Halle, one of the largest in Germany. This post he filled with eminent success until he reached the age of seventy, when he retired from active professional life, and has since devoted himself almost entirely to his historical studies.

While at Zürich, von Lippmann was one of three, later the only listener, to a two-year course of lectures on the history of chemistry. The interest aroused by Professor W. Weith never faded; on the contrary, the fire grew and the great sugar technologist in time developed a reputation as an historian that doubtless will endure long after his technical achievements are forgotten. As was natural, he began with the history of sugar, but this led him into topics of more general interest. A score of important books and hundreds of periodical articles have come from his pen. A perusal of the titles of his writings reveals an astounding catholicity of interests, an examination of the documentation shows the amazing breadth of his reading, and yet most of his work is successfully geared to the capabilities of the average chemist who is merely a layman in matters historical.

The most important of his books are: "Chemie der Zuckerarten;" "Geschichte des Zuckers;" "Geschichte des Wismuts;" "Geschichte der Magnetnadel bis 1200;" "Urzeugung und Lebenskraft;" and the monumental "Entstehung und Ausbreitung der Alchemie."

In 1927, an international Festschrift was issued in honor of his seventieth birthday, and several Americans were proud to participate in this testimonial. From 1925 to 1933 he served as honorary professor of history of chemistry at the University of Halle. He is a member of the academies of Leipzig and Halle, honorary member of many learned societies, degrees have been conferred on him by several universities, the first Sudhoff and Coste medals were awarded to him, and the Berlin Academy of Sciences honored him with its highest distinction, the Leibnitz Medal.

*(Contributed by Ralph E. Oesper, University of Cincinnati.)*

* See frontispiece.

# *The* CALCULATION *of the* MAXIMUM RESULTS OBTAINABLE *by* EXTRACTION *with* IMMISCIBLE SOLVENTS

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THE problem of extracting a material from one phase to another has received attention for a considerable period of time. As early as 1868 Bunsen (*1*) treated the washing of precipitates on the hypothesis that the precipitate retained a constant volume of wash water which in turn contained the soluble impurity. He showed that for a fixed total quantity of wash water the most efficient procedure is to wash successively with small portions of the water rather than to wash with all the water at one time; furthermore, he developed an explicit formula giving the result of washing with $n$ successive portions and established the limiting value of this washing process by considering the case in which $n$ approaches infinity. With the enunciation of the Nernst partition law for the distribution of a solute between two immiscible solvents it becomes evident that Bunsen's work also applies formally to this situation, the precipitate corresponding to the solute phase since it retains a fixed amount of the wash liquor, while the filtrate corresponds to the solvent phase. The equations for this situation, similar to Bunsen's, have been given recently by Griffin (*2*), while an equation for the continuous washing of a precipitate, somewhat analogous to Bunsen's division of the wash water into an infinite number of portions, has been developed and experimentally verified by Rhodes (*3*).

The foregoing cases are illustrations of the so-called multiple-contact method of washing or extraction. Besides this method there is, of course, the countercurrent method. This latter method is the more efficient, but also the more difficult to realize in the laboratory, which probably accounts for the fact that it was not until 1913 that van Ginneken (*4*) developed the equations for the countercurrent washing of a precipitate. In 1917 Hawley (*5*) also gave a good account of this subject. The presentation of the similar equations for countercurrent liquid extraction did not occur until 1932, at which time Hunter and Nash (*6*) developed this aspect of the subject. (It is interesting to note that these same equations have also been developed in connection with stripping of crude oil.) Recently, considerable interest has developed in these extraction processes, largely as a result of the success achieved in the manufacture of quality lubricating oils by solvent extraction.

It will be observed that in the situations discussed so far two restrictions have been imposed: (1) the solvents are immiscible, (2) the partition coefficient is a constant, *i. e.*, the concentration of the solute in the one phase is proportional to its concentration in the other phase. Removing either of these restrictions leads in general to the condition that explicit solutions to the equations representing the results of extraction processes no longer can be obtained. In these cases recourse must be had to graphical methods, to which full references may be found in a recent article by Hunter and Nash (*7*). While the restriction of immiscibility necessarily removes the system under consideration from exact correspondence with any actual system, nevertheless such an immiscible solvent pair may be regarded as an ideal pair, or a limit which many actual systems approach. Consequently, the study of such systems is valuable since the results obtained are applicable, at least qualitatively, to numerous solvent pairs which are nearly immiscible. Accepting the immiscibility restriction and examining, for example, the case in which the concentration of the solute in one phase is proportional to the square of its concentration in the other phase (a common case which arises when the solute exists largely in the form of single molecules in one phase and double molecules in the other), it is found that on attempting to calculate the amount of solute removed by extracting an original solution with $n$ successive batches of fresh solvent no general result can be obtained. Instead, as Friedrichs (*8*) has shown, it is only possible to express the result of $n$ such successive extractions in terms of the result of $n - 1$ such extractions. In other words, it is necessary to calculate the result step by step. However, as will be shown below, it is possible to calculate easily and directly for cases of this general nature the limiting extraction possible if a given volume of solvent is subdivided into $n$ portions, and these portions are used successively to extract the original solution, $n$ being made to approach infinity. This result is somewhat surprising at first glance, since it means that while it is difficult, or at least tedious, to evaluate mathematically the extraction possible by division into say five portions, nevertheless the maximum possible extraction, corresponding to infinite subdivision, may be easily obtained. A further point of interest arises

from the fact that while graphical treatment of this case leads easily to the numerical calculation of the extraction possible for a moderate number of subdivisions, such graphical treatment is not suitable for infinite subdivision (*9*). This aspect of the problem apparently has not been developed generally heretofore although a start has been made (*8*). Inasmuch as these results are interesting by themselves, and also because they tend to complete the calculations possible in such systems, the details are presented in the following.

Suppose that originally there is a solution consisting of $L$ grams of a first solvent containing $y_0$ grams of solute per gram of solvent. There is also available a quantity $U$ grams of a second immiscible solvent with which it is proposed to extract this solution. The operation is to be conducted in the multiple contact fashion, *i. e.*, the $U$ grams are to be subdivided and the solution extracted successively with these smaller portions. The maximum extraction possible will evidently occur when the extracting solvent is divided into an infinite number of infinitesimal portions, and this degree of extraction will represent the limit which could be approached in practice. To establish this limit, let $x$ represent the concentration of solute in the extracting solvent (expressed as grams solute per gram of solvent) which is in equilibrium with a concentration $y$ in the solution, and suppose $x$ and $y$ are connected by a relation $y = kx^n (n > 0)$. (If the ordinary partition law holds, $n = 1$.) If now a differential amount $dU$ of solvent is used, the corresponding change $dy$ is obtained by a material balance:

$$-Ldy = xdU = \left(\frac{y}{k}\right)^{1/n} dU.$$

To obtain the total change in $y$ due to complete use of $U$, this equation must be integrated between the limits $y = y_0$, $y = y$, and $U = 0$, $U = U$. This gives:

$$y_0^{\frac{n-1}{n}} - y^{\frac{n-1}{n}} = \frac{(n-1)U}{Lnk^{1/n}} \quad (n \neq 1).$$

Suppose $n$ has the value previously discussed, namely $n = 2$. Then

$$\sqrt{y_0} - \sqrt{y} = \frac{U}{2L\sqrt{k}}, \text{ whence } y = y_0 - \frac{U}{L}\sqrt{\frac{y_0}{k}} + \frac{U^2}{4L^2k}.$$

For complete solute removal, $y = 0$. Substituting this value, it is found that $U = 2L\sqrt{y_0 k}$. In other words, in this case a finite quantity of the extracting solvent will effect complete removal of the solute. This conclusion is readily seen to be valid for all values of $n$ greater than one.

On the other hand, suppose the solvents are such that $y = k\sqrt{x}$, so that $n = 1/2$. In this case the general formula gives

$$\frac{1}{y_0} - \frac{1}{y} = \frac{-U}{Lk^2}, \text{ whence } y = \frac{y_0 Lk^2}{Lk^2 + y_0 U}.$$

It is apparent that complete extraction, making $y = 0$, is only obtained by having $U = \infty$. In other words, for this case complete solute removal is impossible with a finite amount of solvent. The fraction of solute removed is given by

$$1 - \frac{y}{y_0} = \frac{y_0 U}{y_0 U + k^2 L}.$$

A similar conclusion with regard to complete solute removal is seen to hold for all values of $n$ between zero and one.

The excepted case, $n = 1$, leads to a formula equivalent to that obtained by Griffin, who, however, evaluated the limit directly for this case:

$$\log_e \frac{y}{y_0} = -\frac{U}{kL}, \text{ or } \frac{y}{y_0} = e^{-U/kL}.$$

Upon examination of the degree of extraction possible in this case, it is seen that $y$ can equal zero only if $U = \infty$. Hence this case is similar to those considered for values of $n$ less than one. This rather surprising difference in the degree of extraction obtainable with a finite amount of solvent as $n$ passes through the value one is apparently due to the fact that the curves $y = kx^n$ have a slope of zero at the origin if $n$ is greater than one, while they have a finite slope for $n = 1$ and an infinite slope for values of $n$ between zero and one. The way in which the shape of these curves in the neighborhood of the origin influences the extraction is best visualized by reference to the graphical treatment of this case (*9*).

It is apparent that while the above calculations have been made for a relationship of the form $y = kx^n$, a similar calculation is possible for any functional relationship so long as the integral involved can be evaluated, either explicitly or graphically.

Upon examining the corresponding cases for countercurrent extraction somewhat similar results are obtained. If $n$ is equal to or greater than one, and an infinite number of plates or stages are used, it is found that the final extract leaves at equilibrium with the incoming solution to be extracted unless the ratio (incoming solvent): (incoming solute) is so high that such an exit concentration would carry more material from the system than enters it. For example, suppose $y = kx^2$ and take $L = 1$. Then, if the entering solute concentration is $y_0$, the solute concentration in the extract is $\sqrt{\frac{y_0}{k}}$ provided $U\sqrt{\frac{y_0}{k}}$ (which is the amount of solute removed by the solvent) is not greater than $y_0$ (the amount of solute which has entered the system during the period this extract has been removed). Hence, if $U\sqrt{\frac{y_0}{k}} = y_0$, or $U = \sqrt{ky_0}$, all the solute will be extracted, while for smaller values of $U$ complete extraction is obviously impossible. Larger values of $U$ will evidently lead to complete extraction, although the resulting extract will necessarily be less concentrated since the same amount of solute leaves in a larger volume of solvent.

For values of $n$ less than one it is found, similar to the multiple extraction situation, that complete extraction

can be secured only by use of an infinite amount of solvent. This case is best handled graphically (*9*). For example, in Figure 1 is given a typical equilibrium curve of this type. Let $y_0$, as before, be the concentration of the entering solute, and $y_1$ the final concentration in the extracted solution. To locate $y_1$ a line is drawn having a slope $U/L$ and lying as close to the equilibrium curve as possible, but at the same time lying to the left of the curve for all points below $y = y_0$. The intersection of this line with the $y$ axis gives $y_1$. It is seen that for this case a tangent is the closest line which can be drawn. If, however, $y_0$ lies below the point of tangency for a line of this slope, as indicated by $y_0'$, then a secant passing through $y_0$ and having the slope $U/L$ is the desired line, as shown by the broken line.

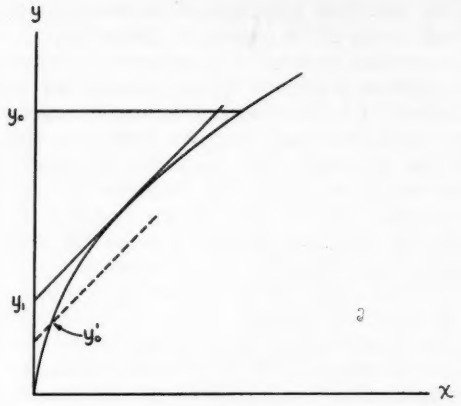


FIGURE 1

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# A SIMPLE EXPERIMENT IN CHROMIUM PLATING

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CHROMIUM plating has recently become so important commercially that students desire to know more about the process than they read in the text. At present, none of the many laboratory manuals or textbooks referred to for this topic contain any exercise on chromium plating that could be used in a high-school demonstration or laboratory. It was in order to satisfy the need for a simple experiment on this process that this laboratory exercise was devised. The exercise has proved to be a practical one to perform because of the comparative cheapness of materials and simplicity of preparation and set-up.

This experiment may be used either as a demonstration or as a laboratory exercise. If used as a laboratory exercise, one set-up may be prepared for each group of two or three students. Each pupil should prepare and polish his own individual strip of copper for chromium plating. Some students may even find time during the same laboratory period to chromeplate a strip of brass or nickel as an additional application of this lesson.

*Apparatus.*—Four dry cells (1.5 volts each), one ordinary glass tumbler, two spring-type battery clips, strip of sheet lead 1″ × 4″, strip of sheet copper 1″ × 4″, fine steel wool, soft cheesecloth, copper wire.

*Chemicals.*—Twenty-five grams of chromic anhydride, concentrated sulfuric acid.

*Method.*—Clean the copper strip for electroplating by immersing it in concentrated sulfuric acid for $^1/_2$ to 5 minutes, depending on the initial cleanliness of the copper. Wash off all the acid with water. Impart a high polish to the copper by rubbing, first with fine steel wool, and then with soft cheesecloth. Since the chromium adheres better to a thoroughly clean surface, much care must be taken in this operation.

Prepare the electrolytic bath by dissolving in the glass tumbler the 25 grams of chromic anhydride in 100 cc. of water. Acidify this solution with 3 drops of concentrated sulfuric acid. This bath may be prepared as a stock solution and used over and over again. After hooking up the four dry cells in series, connect the lead strip to the positive terminal of your battery. Use one of the spring-type battery clips to fasten the lead electrode to the side of the glass tumbler. Using some copper wire and the other battery clip, connect the copper strip to the negative terminal. Place a wooden splint across the top of the tumbler so that when the bent copper strip is hung on it, the strip (cathode) will dip into the electrolyte about $1^1/_2$″ away from, and parallel to, the lead anode. Allow the copper to remain in the solution for about 20 to 30 seconds. Then remove it from the bath, wash with water, and dry and polish with cheesecloth.

*It is only as we learn about the materials, forces, and operations of the world in which we live that we can wisely adapt ourselves to life in it and use these materials and forces to our own advantage. Pure science seeks to gain this knowledge and applied science, or engineering, seeks to use it in desirable ways. The two go hand in hand, and together their success epitomizes man's continual ascent to a richer, fuller, more satisfying life.*—KARL T. COMPTON

# *A* CARBON DIOXIDE "GENERATOR"

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FOR the past two years this laboratory has used solid carbon dioxide as a source of gas for the preparation of sodium bicarbonate. The accompanying diagram, Figure 1, shows the arrangement of apparatus that has proved successful in the hands of first-year students. The bottle containing the solid carbon dioxide is fitted with a tight rubber stopper carrying a Bunsen valve and a delivery tube. It is usually necessary to wire the stopper in place. The Bunsen valve is closed at the top with a spring pinch-clamp.

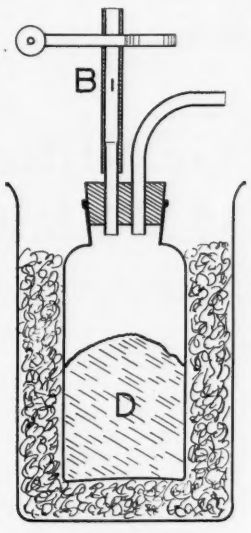


FIGURE 1.—THE CARBON DIOXIDE GENERATOR

*B*—Bunsen valve
*D*—Dry ice

The rate of sublimation (generation) may be controlled by varying the amount of insulation as well as the type of container. A 250-cc. bottle filled with dry ice and wrapped with a loosely wound towel, held in place with a beaker as shown in the diagram, will furnish a steady supply of gas for ten hours at the rate of about one-half mole per hour. A metal container (tin can) standing in air at room temperature will supply the gas at the rate of about two moles per hour. With the aid of these figures one may easily design a container that will furnish gas at the desired rate.

The Bunsen valve is the important part of the apparatus and the safety of the experimenter depends upon its successful operation. Students are directed to make a slit $^1/_8$–$^1/_4$ inch in length along the wall of a rubber tube.* A file point should be inserted through the opening, from the inside, to make certain that the slit actually goes through the wall of the tube. The top of the tube is closed with a spring pinchclamp rather than a glass plug, since it was found that students may push the glass past the slit and thereby prevent the escape of the gas. Because of the great danger involved when solid carbon dioxide is placed in a closed container each valve should be tested by means of a manometer. In this laboratory a mercury manometer, Figure 2, was set up with sufficient height to balance the pressure in the compressed air line used to test the release pressure of the valve. In order to prevent too sudden pressure changes, a capillary tube† was inserted between the air line and the manometer. This arrangement has been entirely satisfactory for student use.

In short, this apparatus will furnish at a reasonable cost a steady source of carbon dioxide gas at a constant pressure for several hours without attention or adjustment.

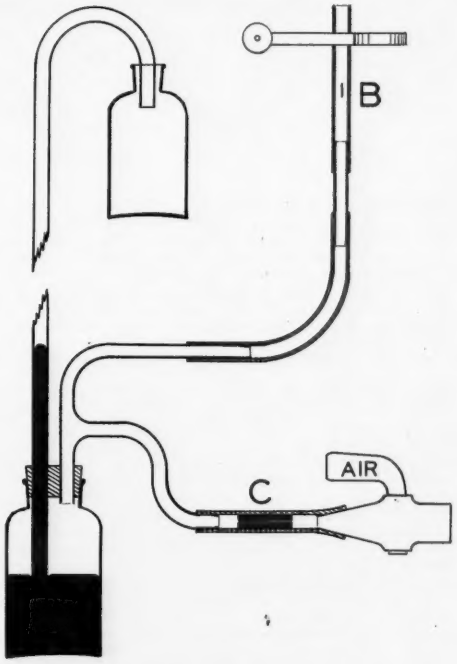


FIGURE 2.—THE MANOMETER

*B*—Bunsen valve
*C*—Thermometer tubing

*Note:*—The increased industrial use of "dry ice" has brought the cost of carbon dioxide gas from this source below the cost of material for the marble-hydrochloric acid method. Our records show that the cost of marble chips and hydrochloric acid used in the generation of carbon dioxide for the preparation of sodium bicarbonate was over ten cents per student, whereas the dry ice cost about four cents per student.

The cost of dry ice depends somewhat on the locality. How-

* The tubing used was the laboratory quality red tubing, $^1/_4$-inch diameter and $^1/_{16}$-inch wall. Valves made of this tubing maintained pressures between ten and twenty-five cm. of mercury.

† One inch of a broken thermometer tube allows a flow of air which corresponds to the flow of carbon dioxide from the generator.

ever, the standard fifty-pound cakes may be obtained almost anywhere in the United States at a maximum cost of five cents per pound. The consumer should calculate on a fifteen per cent. shipping loss per twenty-four hours. Shipment is usually made by truck or railway express. Information regarding the location of shipping points may be obtained by writing to the offices of the Liquid Carbonic Corporation, 52 Vanderbilt Avenue, New York City. Cutting the fifty-pound blocks adds considerably to the expense and the local ice cream stores may be of service in filling small orders.

The dry ice may be stored cheaply and conveniently in a nest of three or four concentric pasteboard cartons separated by excelsior. It may be broken up either in a laboratory ice crusher or by pounding it in a cloth bag with a mallet.

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*Volume* **1** *(1909) through* **26** *(1934)*

HUBERT N. ALYEA

Princeton University, Princeton, New Jersey

‡301. **The manufacture of oil of lemon and citrate of lime in Sicily.** E. M. CHACE. *Ind. Eng. Chem.*, **1**, 18–27 (1909).—Geographical location of lemon factories, sponge and machine method of producing lemon oil, citrate of lime machinery. 1 map, 11 pictures. *Popular: raw materials, products, little chemistry. 2 hrs.*

302. **The rare earths—their production and application.** H. S. MINER AND M. C. WHITAKER. *Ind. Eng. Chem.*, **1**, 235–45 (1909).—Occurrence of monazite sand, history of gas illumination, Auer's thoria-ceria mantle, industrial production of mantles. 1 portrait, 7 pictures. *Popular: historical, raw materials, processes, products. 2 hrs. 50 min.*

*303. **The Perkin Medal Award to C. M. Hall.** *Ind. Eng. Chem.*, **3**, 143–51 (1911).—C. F. MCKENNA: meaning of the Perkin Medal. C. F. CHANDLER: history of production of aluminum. C. M. HALL: history of his discovery, financial dealings. Remarks by P. E. HEROULT, T. W. RICHARDS, and others. 1 picture. *Popular: historical, processes. Chemical: research. 2 hrs. 30 min.*

304. **The centenary of glucose and the early history of starch.** B. HERSTEIN. *Ind. Eng. Chem.*, **3**, 158–68 (1911).—Starch before the nineteenth century, dextrin, Kirchhof discovers conversion of starch to sugar by acids, his priority disputed, industrial application, theory of reaction, cost of starch sugar, glucose in England and America, development since 1820. *Popular: historical, raw materials, processes, products, economics, no organic required. Chemical: research. 3 hrs. 15 min.*

305. **Research as a financial asset.** W. R. WHITNEY. *Ind. Eng. Chem.*, **3**, 429–33 (1911).—Increasing uses of chemical compounds, metals, what a research laboratory does, interrelation of problems in different research laboratories, difficulty to measure economic value of research, research work in German, English, and American industries. *Popular: products, economics. Chemical: research. 1 hr. 30 min.*

*306. **The earning power of chemistry.** A. D. LITTLE. *Ind. Eng. Chem.*, **3**, 598–607 (1911).—Contributions to civilization such as liquid air, Davy lamp, pure water, fertilizers, textiles, lighting; earning power of chemical research in preventing industrial waste, and replacing costly processes. *Popular: historical, raw materials, processes, products, economics. Chemical: research. 2 hrs. 10 min.*

*307. **Mineral wastes: the chemists' opportunity.** C. L. PARSONS. *Ind. Eng. Chem.*, **4**, 125–31 (1912).—Economy suggested by chemical research in a number of industries including steel, flue dust, fertilizer, mining, coal, low-grade ores, possible uses for many rare elements, immense ore deposits, alloys, value of research. *Popular: raw materials, processes, products, properties, economics. 2 hrs. 10 min.*

*308. **Perkin Medal Award to H. Frasch.** *Ind. Eng. Chem.*, **4**, 132–47 (1912).—C. F. CHANDLER: presentation address, historical résumé of Frasch's accomplishments. H. FRASCH: types of oil, desulfurization, roasting, California oil, the first attempt to obtain sulfur by the Frasch process, difficulties with the Anglo-Sicilian Company. A. F. LUCAS: geology of sulfur and sulfur oil deposits of the coastal plain. F. H. POUGH: sulfur mines of the Union Sulfur Company in Louisiana, with details of equipment design. 1 portrait, 4 pictures. *Popular: historical, raw materials, processes, properties, economics. Chemical: research. Pages 134–40 and 143–7 recommended. 4 hrs. 30 min.*

309. **Miscellaneous mineral wastes.** C. L. PARSONS. *Ind. Eng. Chem.*, **4**, 185–8 (1912).—Need to prevent waste of material by faulty industrial processes, numerous elements and a few substances being briefly described. *Popular: raw materials, properties, economics. 1 hr. 20 min.*

310. **Perkin Medal Award to J. Gayley.** *Ind. Eng. Chem.*, **5**, 241–9 (1913).—C. F. CHANDLER: presentation address. J. GAYLEY: **Development of the dry air blast and its industrial success.** H. M. HOWE: the value of Gayley's expert opinions. E. HART: Dr. Gayley's interest in education at Lafayette College. 1 portrait, 2 figures, 1 graph. *Engineering: historical, processes, equipment design (process not universally approved today). 2 hrs. 20 min.*

311. **The production of synthetic ammonia.** F. HABER AND R. LE ROSSIGNOL. *Ind. Eng. Chem.*, **5**, 328–31 (1913).—Equilibrium conditions of temperature and pressure, structural details of catalyst chamber, uranium and osmium catalysts. 4 figures. *Chemical: advanced. Engineering: equipment design. 50 min.*

*312. **Synthesis of precious stones.** I. H. LEVIN. *Ind. Eng. Chem.*, **5**, 495–500 (1913).—Types of precious stones and methods of producing diamonds, emeralds, rubies, and sapphires. 6 pictures, 2 figures. *Popular: historical, processes, products. Chemical: research. 1 hr. 20 min.*

313. **Perkin Medal Award to J. W. Hyatt.** *Ind. Eng. Chem.*, **6**, 155–62 (1914).—G. W. THOMPSON: presentation address, scientific imagination, Hyatt's life history, the patents on celluloid, the Parks and Spill patent. J. W. HYATT: discovery of celluloid, industrial development, sugar-cane mill. F. VANDERPOOL: personal reminiscences of the Hyatt brothers. 1 portrait. *Popular: historical, processes, products, properties, no organic required. Chemical: research. 2 hrs. 30 min.*

314. **Modern chemical industry.** F. HABER. *Ind. Eng. Chem.*, **6**, 325–30 (1914).—Zirconium oxide in place of stannic oxide in the enamel industry, mesothorium from monazite sand, blast lamp and Bunsen burner flame, manufacture of formic and oxalic acids by

* Contribution from the Frick Chemical Laboratory of Princeton University.

† The purpose of this bibliography and its method of compilation are outlined in Part I, J. CHEM. EDUC., **13**, 76–81 (1936).

‡ Numbers 1–300 are reserved for *Chemical & Metallurgical Engineering;* numbers 301–600, assigned to *Industrial and Engineering Chemistry.*

combustion, fixation of nitrogen, oxidation of nitrogen, synthesis of ammonia. *Chemical: processes, research. 2 hrs.*

315. **The war and the chemical industry.** WM. H. NICHOLS. *Ind. Eng. Chem.*, **7**, 1316 (1915).—Résumé of chemical industries in United States up to time of World War, political obstacles to progress of American industry. See also, A. D. LITTLE. **The dyestuff situation and its lesson.** *Ibid.*, 237–9. Contrast between American and German coal-tar color industries. *Popular: economics, little chemistry. 2 hrs. 40 min.*

316. **Perkin Medal Award to E. Weston.** *Ind. Eng. Chem.*, **7**, 243–54 (1915).—C. F. CHANDLER: presentation address, Weston's life history. L. H. BAEKELAND: Edward Weston's inventions. E. WESTON: electroplating nickel; dynamos, the arc light, carbon filament lamps, alloys for electrical work, the standard cadmium cell. C. HERING: some of Dr. Edward Weston's achievements in the field of electricity. 1 portrait. *Popular: historical, processes, properties. Chemical: research. 3 hrs. 45 min.*

317. **Extraction and recovery of radium, uranium and vanadium from carnotite.** C. L. PARSONS, R. B. MOORE, S. C. LIND, AND O. C. SCHAEFER. *Ind. Eng. Chem.*, **8**, 48–53 (1916).—Treatment of ore, refining radium, purifying uranium, recovering vanadium, percentage yields, cost. 6 pictures. *Chemical: processes. Engineering: equipment design, economics. See also pages 284, 469, 660. 1 hr. 30 min.*

318. **Perkin Medal Award to L. H. Baekeland.** *Ind. Eng. Chem.*, **8**, 177–90 (1916).—W. M. GROSVENOR: introductory address, former medalists. C. F. CHANDLER: presentation address, industrial processes developed by American chemists, bakelite, Baekeland's patents. R. A. ANTHONY: the discovery of Dr. Baekeland. E. H. HOOKER: an appreciation of Dr. Baekeland. L. H. BAEKELAND: **Practical life as a complement to university education.** History of velox, uncertainties of patents, electrolytic soda, synthetic resins, and bakelite, developing a new chemical industry, American banks ill-prepared for new chemical enterprises. 1 portrait. *Popular: historical, products, properties, economics, no organic required. Chemical: research. 4 hrs. 20 min.*

319. **The war and American chemical industry.** R. F. BACON. *Ind. Eng. Chem.* **8**, 547–53 (1916).—War influences on industry; manufactured products formerly imported from Europe, such as coal-tar products, carbolic acid, naphthalene, dyes, potash, barium products; effect of war on industries producing mineral acids, ammonium sulfate, sodium compounds, glass, carbon, chlorides, oxalic acid, special steels, zinc, tin, aluminum, antimony, and mercury; industrial preparedness. *Popular: raw materials, processes, economics. 2 hrs. 20 min.*

*320. **Willard Gibbs Medal Award to W. R. Whitney.** *Ind. Eng. Chem.*, **8**, 559–64 (1916).—G. THURNAUER: presentation address, research in the General Electric Company under the guidance of Dr. Whitney. W. R. WHITNEY: **Incidents of applied research.** Status of applied research in America and in the General Electric Company, unexpectedness of new knowledge; research on carbon arcs, high vacuum, tungsten filament lamps, argon lamps, need for students in chemical science in America. 1 portrait. *Popular: products, properties. Chemical: research. 2 hrs.*

321. **The metallurgy of the rarer metals.** J. W. RICHARDS. *Ind. Eng. Chem.*, **8**, 736–40 (1916).—Method and cost of production, possible uses for beryllium, magnesium, alkaline earths, boron, chromium, titanium, molybdenum, zirconium, cerium. *Popular: raw materials, products, properties, economics. Chemical. 1 hr. 40 min.*

322. **Perkin Medal Award to E. Twitchell.** *Ind. Eng. Chem.*, **9**, 192–9 (1917).—J. ALEXANDER: introductory address, medalist's inventions in the U. S. and abroad. C. F. CHANDLER: presentation address. E. TWITCHELL: his discovery of a special catalyst for hydrolyzing fats, experiments performed, other applications of his catalysts. A. C. LANGMUIR: the Twitchell process and the glycerin trade. M. ITTNER: the Twitchell process in the soap and candle industry. H. SCHMIDT: an appreciation of Dr. Twitchell, anecdotes. 1 portrait. *Popular: historical, processes, no organic required. Chemical: research. 1 hr. 5 min.*

323. **Chemical industry in Canada.** H. E. HOWE. *Ind. Eng. Chem.*, **9**, 548–51 (1917).—Chemical production, drugs and dyes, wood products, research organizations; Canadian resources: agriculture, forests, minerals, game, water power, fuel; need for coöperation with U. S. *Popular: raw materials, economics. 35 min.*

*324. **New alloys to replace platinum.** F. A. FAHRENWALD. *Ind. Eng. Chem.*, **9**, 590–7 (1917).—Production, market, and uses of platinum; specifications for a substitute, possible elements discussed from their position in the periodic table; alloys tested for chemical, physical, electrical, and thermal properties, and use for jewelry and dental work. 1 chart. *Popular: raw materials, properties. Chemical: research. 1 hr. 15 min.*

325. **On the relation between the physical properties and chemical compositions of glass. VII-Etch figures.** E. W. TILLOTSON, JR. *Ind. Eng. Chem.*, **9**, 937–41 (1917).—Discovery of, and theories concerning, etch figures; photomicrographs and experiments which prove etch figures are crystals deposited on the glass, not an uneven eating away of the glass. 20 pictures. *Chemical: historical, properties, research. 30 min.*

*326. **Chemical microscopy.** E. M. CHAMOT. *Ind. Eng. Chem.*, **10**, 60–6 (1918).—Microscopic methods not appreciated, stand by American-made instruments; ease, cheapness, and quickness of microscopy in organic analysis, melting-point determinations, and applications in cement, ceramics, foods, metallurgy, paints, paper, and textiles. 10 pictures. *Popular: processes. Chemical: research. 1 hr.*

327. **The potteries at Shek Woan near Canton, China.** C. N. LAIRD. *Ind. Eng. Chem.*, **10**, 568–71 (1918).—Mixing the batch; forming articles on the wheel, mold, and by hand; coloring with copper, cobalt, and lead; kiln firing; organization of the village. 6 pictures. *Popular: raw materials, processes, products, economics. 30 min.*

328. **Potash from Searles Lake.** A. DE ROPP, JR. *Ind. Eng. Chem.*, **10**, 839–44 (1918).—Geographical locations of salt deposits, equipment for pumping, and evaporating brine. 3 maps, 11 pictures. *Engineering: processes, equipment design, raw materials. 30 min.*

329. **Perkin Medal Award to F. G. Cottrell.** *Ind. Eng. Chem.*, **11**, 147–54 (1919).—C. F. CHANDLER: presentation address, widespread application of Cottrell precipitator. F. G. COTTRELL: **Industrial liquefaction and separation of permanent gases.** Oxygen, helium, and other rare gases; patent difficulties, Navy appropriations and control during the great war. B. SPEED: an appreciation of Dr. Cottrell. Bibliography. 1 portrait. *Popular: historical, economics, research (not much about electrical precipitation). 1 hr. 10 min.*

330. **Chlorine adsorption and the chlorination of water.** A. WOLMAN AND L. H. ENSLOW. *Ind. Eng. Chem.*, **11**, 209–13 (1919).—Inadequate city control of chlorination; chlorine adsorption: amount available, rate of adsorption, color, turbidity, oxygen consumed; effective disinfectant dosage, with opinions of others; 5 or 30 minute adsorption tests. 3 graphs, 4 tables. *Chemical: properties, research. 50 min.*

331. **Report of the alien property custodian.** A. M. PALMER. *Ind. Eng. Chem.*, **11**, 352–65 (1919).—History of German chemical industry, especially dyes and drugs, economic structure, its control of American industry, wartime economic activities, stock transactions, protective actions of the Chemical Foundation. *Popular: historical, economics. 2 hrs. 15 min.*

*332. **The American spirit in chemistry.** E. F. SMITH. *Ind. Eng. Chem.*, **11**, 405–10 (1919).—Young followers of Joseph Priestley: Woodhouse, baking-chemist; Robert Hare's electric furnace and other researches, excerpts from scientific journals of their time, their magnificent spirit. 12 pictures. *Popular: historical, processes, research. 50 min.*

333. **Chemistry in the Navy.** R. EARLE. *Ind. Eng. Chem.*, **11**, 924–7 (1919).—New products: flashless powder, special explosives, new motive power for torpedoes, nitrogen fixation, helium for balloons, special alloys, pyrotechnics, gas and gas masks. 1 picture. *Popular: products, properties, research. 40 min.*

334. **Perkin Medal Award to C. F. Chandler.** *Ind. Eng. Chem.*, **12**, 183–95 (1920).—M. C. WHITAKER: personalities. M. T. BOGERT: presentation address, Chandler's life history as a student, educator, industrial chemist, founder, and public servant. C. F. CHANDLER: life history; investigations of kerosene, drinking waters, poisonous cosmetics. 1 portrait. *Popular: historical, properties, research. Conversational. 2 hrs. 10 min.*

*335. **The Chandler lecture. Medal address: the littlest things in chemistry.** W. R. WHITNEY. *Ind. Eng. Chem.*, **12**, 599-608 (1920).—Suspension in liquids; colloids, dimensions of molecules, studies *in vacuo;* electrons in electrolysis, luminescence, and wireless; gas ionization, electric arcs, atomic structure: X-ray spectra, quanta, valency; isotopes and canal rays. 1 portrait. *Popular: properties. Chemical: research. 1 hr. 20 min.*

336. **The direct synthetic ammonia process.** R. S. TOUR. *Ind. Eng. Chem.*, **12**, 844–52 (1920).—Equilibrium conditions for Haber process, production of water-gas and producer-gas; oxidation of carbon monoxide, catalysts used; purification of hydrogen by removing oxides of carbon; ammonia synthesis: gas composition, heat interchange and catalysis, removal of ammonia, circulation of gas, operating quantities, operation at Sheffield, Alabama. 6 pictures. 1 flow-sheet. *Chemical: processes, properties. Engineering: economics, equipment design. 1 hr. 10 min.*

337. **(Research problems): National Research Council report of the chairman at the annual meeting of the Division of Chemistry and Chemical Technology.** *Ind. Eng. Chem.*, **12**, 911–8 (1920).—Baking, turpentine, protoplasm, war gases, special sugars, normal weight, structural rocks, clay, pressure phenomena inside the earth, thunder-storms, surface colors, Brownian movement, adsorption of gases, criteria of purity, quicksands, metallic luster, educational tests, conclusions. *Popular: products, properties. Chemical: research. 1 hr. 5 min.*

*338. **Perkin Medal Award to W. R. Whitney.** *Ind. Eng. Chem.*, **13**, 158–66 (1921).—A. D. LITTLE: Willis R. Whitney, his devotion to research, his inspiration. C. F. CHANDLER: presentation address, products of the General Electric Research Laboratory, Whitney's publications. W. R. WHITNEY: **The biggest things in chemistry.** Experiences as a student; bigger things include widening scope of chemistry, productive teaching, new alloys; organic, agricultural, and medical research; growth of mind and religious understanding. 1 portrait. *Popular: historical, philosophical. Chemical: research. 1 hr. 15 min.*

*339. **The American potash industry and its problems.** J. E. TEEPLE. *Ind. Eng. Chem.*, **13**, 249–52 (1921).—Consumption, production, and location of potash in the U. S.; Searles Lake deposits, equilibrium diagrams, double salts, separation of potash from borax,

overcoming foaming during evaporation, vacuum distillation, other problems, need for tariff protection. *Chemical: raw materials, processes, economics, research. 40 min.*

340. **The place of chemistry in business.** A. D. LITTLE. *Ind. Eng. Chem.*, **13**, 386–90 (1921).—Service of chemistry in agriculture, antitoxins, transportation, abrasive, sulfur, oil refining, dynamo, gold mining, and explosive industries; industries at Niagara Falls; chemistry in reconstruction, an aid to the manufacturer. 1 portrait. *Popular: products, economics. Chemical: research. 40 min.*

341. **Incendiaries in modern warfare.** A. B. RAY. Part I: *Ind. Eng. Chem.*, **13**, 641–6 (1921).—Chemical composition of incendiary materials including phosphorus, thermite, oxidizing agent-combustible mixtures, flammable solids and liquids, "solid oil," spontaneously flammable liquids. *Popular: historical, products, properties. Chemical: research. 1 hr. 50 min.*

342. **Chemistry and the state.** F. P. GARVAN. *Ind. Eng. Chem.*, **13**, 866–73 (1921).—German activity in setting up coal-tar industries, drug boycott, U. S. industry must be protected, research laboratories to be erected; chemistry and war, war materials, future weapons; the creative chemist's task. 1 portrait. *Popular: historical, products, economics, propaganda. 1 hr. 10 min.*

343. **Pyrex: a triumph for chemical research and industry.** W. H. CURTIS. *Ind. Eng. Chem.*, **14**, 336–7 (1922).—History of development of pyrex glass with superior mechanical strength and temperature resistance by Corning Glass Works. *Popular: properties, research. 20 min.*

344. **The flower and the organic chemist: perfumes—natural and synthetic.** M. T. BOGERT. *Ind. Eng. Chem.*, **14**, 359–64 (1922).—9 types of odors, amazing sensitivity of olfactory organs, historical importance of perfumes; preparation by mechanical methods, distillation with steam, extraction with volatile solvents, enfleurage; production in France. 1 portrait. *Popular: historical, raw materials, processes, products, economics. 50 min.*

345. **The manufacture of reflecting telescope discs.** D. E. SHARP AND W. H. RISING. *Ind. Eng. Chem.*, **14**, 511–5 (1922).—Equipment for casting 40-inch discs, the mold; electric and gas furnaces, casting, advantage of low expansion glass. 4 pictures, 2 figures, 1 graph. *Engineering: equipment design. 40 min.*

*346. **Chandler Medal Award to E. F. Smith.** *Ind. Eng. Chem.*, **14**, 556–60 (1922).—E. F. SMITH: **Samuel Latham Mitchell—A father in American chemistry.** Intensely American, champion of phlogiston; septon, universal biochemical decomposer. 2 portraits. *Popular: historical. Chemical: research. 45 min.*

347. **An outline of the history of chemistry symbolically represented in a Rookwood fountain.** H. S. FRY. *Ind. Eng. Chem.*, **14**, 868–72 (1922).—Tenets and accomplishments of famous chemists in prehistoric, alchemical, medicinal, phlogiston and quantitative periods of chemical history richly illustrated. 2 pictures. *Popular: historical. 40 min.*

*348. **The human side of chemistry.** E. E. SLOSSON. *Ind. Eng. Chem.*, **14**, 887–93 (1922).—Large number of new synthetic products, the present revolutionary era of creative science, within the atom, the fuel problem, harnessing the sun; chemistry an agent for democracy, a sociological influence; metaphysics, need for popularization. 1 portrait. *Popular: historical, economics, philosophical. Chemical: research. 1 hr. 10 min.*

*349. **Early chemical industry in America—a few comparisons of past and present conditions.** C. A. BROWNE. *Ind. Eng. Chem.*, **14**, 1066–71 (1922).—Chemical operations carried out by the Indians, French and Spanish smelting, John Winthrop and chemical industries in New England, economic factors, colonial chemical industry stimulated by trouble with England, early struggles for protection, patents. 5 pictures, 1 portrait, 1 graph. *Popular: historical, products, economics. 50 min.*

350. **Photosynthesis and the possible use of solar energy.** H. A. SPOEHR. *Ind. Eng. Chem.*, **14**, 1142–5 (1922).—Photosynthesis, a waste of solar energy; duty of science to preserve available energy sources and discover new ones. *Popular: raw materials, economics. 40 min.*

351. **Ernest Solvay—an appreciation.** W. H. NICHOLS. *Ind. Eng. Chem.*, **14**, 1156–8 (1922).—Boyhood, conception and development of Solvay process. An obituary. 1 portrait. *Popular: historical, little chemistry. 25 min.*

*352. **Robert Brown and the discovery of the Brownian movement.** L. C. NEWBLL. *Ind. Eng. Chem.*, **15**, 1279–81 (1923).—Biographical. Brown's experiments. 1 portrait. *Popular: historical, little chemistry. 50 min.* See also: **Some cartoons of van't Hoff.** R. H. MCKEE. *Ibid.*, 192–3. Sketch. 1 portrait, 6 caricatures. *Popular: historical. 20 min.*

353. **Gulian C. Verplanck's account of alchemy in old New York.** C. A. BROWNE. *Ind. Eng. Chem.*, **16**, 90–1 (1924).—The story of Jan Max-Lichenstein, New York alchemist. *Popular: historical, little chemistry. 30 min.*

354. **Dalton Memorials in Manchester, England.** A. D. THORBURN. *Ind. Eng. Chem.*, **16**, 190–1 (1924).—5 pictures showing Dalton collecting marsh-fire gas, some of his atomic symbols, a statue, and some personal effects. Short legend, and an anecdote. *Popular: historical. 20 min.*

355. **Some early chemical symbols.** E. H. SMITH. *Ind. Eng. Chem.*, **16**, 406–8 (1924).—4 pictures of symbols used in the Middle Ages. *Popular: historical. 20 min.*

*356. **The expansion of chemistry.** E. E. SLOSSON. *Ind. Eng. Chem.*, **16**, 447–50 (1924).—Historical application of chemical tools: vegetable oils for Diesel engines, the Phoenician alphabet, Venetian glass and salted fish, fall of the Hanseatic League when herring deserted the carbon dioxide laden Baltic Sea, rubber; physiological tools: adrenalin, soil bacteria, insulin, sex hormones; muscle fatigue. *Popular: historical, products, properties, biological. 1 hr. 20 min.*

357. **Some high lights of last year.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **16**, 995–1001 (1924).—A review of 1924: insulin, vitamin D, chlorine clinics, iodine; ethylene as anesthetic, for ripening fruit, with oxygen in torches; nitrogen, potash, and phosphate fertilizers; motor fuels, quartz glass, liquid chlorine, bleaching powders, synthetic menthol, artificial silk, nitrocellulose, lacquers, mercury vapor boiler, synthetic phenol, rubber, tear gas, tantalum; frauds. 5 pictures. *Popular: products, properties. Chemical. 2 hrs. 20 min.*

*358. **The fifth estate.** A. D. LITTLE. *Ind. Eng. Chem.*, **16**, 1105–10 (1924).—A philosophical study of the opinions of great scientists who wondered, questioned, generalized, and had the capacity to apply. *Popular: historical, little chemistry. 2 hrs.*

359. **Corrosion of iron.** W. R. WHITNEY. *Ind. Eng. Chem.* **17**, 385–9 (1925).—Chemical corrosion rather than erosion of soft iron, steam turbine buckets, and ship propellors. 9 pictures, 1 figure. *Chemical: research. 1 hr. 20 min.*

360. **Alcohol and human physiology.** F. G. BENEDICT. *Ind. Eng. Chem.*, **17**, 423–6 (1925).—Alcohol as a food, permissible amounts, physiological and psychological tests, use and misuse of alcohol. *Popular: properties, little chemistry, biological. 1 hr. 20 min.*

*361. **The hand-writing on the wall.** A. D. LITTLE. *Ind. Eng. Chem.*, **17**, 857–8 (1925).—Examples of industrial successes and failures because of the presence or absence of a consulting chemical engineer. 1 portrait. *Popular: products, economics. 20 min.*

362. **The twilight zone of matter.** A. FINDLAY. *Ind. Eng. Chem.*, **17**, 891–4 (1925).—Colloid chemistry. Evidence for colloidal particles, adsorption, protective action as in smooth ice cream, biological importance of diffusion and emulsions. *Popular: products, properties, biological. Chemical: processes. 1 hr. 10 min.*

363. **Dust explosions in industrial plants.** H. R. BROWN. *Ind. Eng. Chem.*, **17**, 902–4 (1925).—Precautions for handling dusty material. Types of explosive dusts. 3 pictures. *Popular: properties. 1 hr.*

364. **Twelve months of progress.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **17**, 995–1001 (1925).—A review of 1925. Court decisions, tetraethyl lead health hazard, bromine from sea, chemical warfare, new dyes and medicinals, solvents, hydrocyanic acid fumigation, carbon monoxide poisoning, helium and compressed air, selenium for flameproofing, lacquer developments, nitrogen fixation, acetic acid, growing rubber in the United States, industrial power, new elements, and frauds. *Popular: products, properties. 2 hrs. 20 min.*

365. **Artificial silk.** M. G. LUFT. *Ind. Eng. Chem.*, **17**, 1037–42 (1925).—History; kinds of artificial silk: nitrocellulose, cuprammonium, acetate, and viscose; properties and uses. 5 pictures, 1 graph. *Popular: raw materials, processes, products, properties. Chemical: equations. 2 hrs.*

366. **Screening smokes.** H. W. WALKER. *Ind. Eng. Chem.*, **17**, 1061–5 (1925).—Properties of smoke screens; theoretical equations for cloud travel; formation by explosion, heat and pressure. Materials used: white phosphorus, sulfur trioxide, titanium tetrachloride, silicon tetrachloride, ammonia and water, crude oil, other mixtures; tactical use of smoke. 5 pictures. *Popular: historical, raw materials, products, properties. 1 hr. 30 min.*

367. **Perkin Medal Award to R. B. Moore.** *Ind. Eng. Chem.*, **18**, 203–11 (1926).—R. B. MOORE: **Commercial production of . . . . helium.** History, production from natural gas, repurification, use in airships. 1 portrait, 2 figures, 1 graph. *Popular: historical, raw materials, products. Engineering: equipment design. 2 hrs. 20 min.*

*368. **The romance of carbon.** A. D. LITTLE. *Ind. Eng. Chem.*, **18**, 444–51 (1926).—Soot, charcoal, graphite, famous diamonds, oxides of carbon, carbonate deposits, carbon in organic chemistry: source of energy as coal, gas, asphalt, and petroleum. Excellent résumé. 3 pictures. *Popular: historical, raw materials, products, properties, economics, no organic required. Chemical: research. 2 hrs. 40 min.*

*369. **Industry finds a new tool—X-rays.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **18**, 577–80 (1926).—Study of castings, of atomic and molecular structure; industrial applications at M. I. T. as in strains in metals, resistance to abrasions, tungsten filaments, and ceramics. 5 pictures. *Popular: properties. Chemical: research. 1 hr. 20 min.*

370. **The relation of light to life and health.** W. A. PRICE. *Ind. Eng. Chem.*, **18**, 679–85 (1926).—Chlorophyll and hemoglobin, effect of light on bone formation, calcium metabolism, light-activated cod-liver oil, sunlight in modern life. 8 pictures, 2 graphs. *Popular: properties. Chemical: research. Biological. 2 hrs. 20 min.*

*371. **Fifty years of chemical advance.** *Ind. Eng. Chem.*, **18**, 892–960 (1926).—A series of articles by authorities in the fields of metallurgy, glass-making, water supply and sewerage, rubber, explosives, soap, Portland cement, steel, photography, pulp, artificial lighting, aluminum, silk, textile dyeing, wood distillation, insecticides, aro-

matic chemicals, tanning, petroleum, cottonseed products, fertilizers, glass, gas, paint and varnish, synthetic medicinals, ceramics, standardization and evaluation of medicinals, compressed gases, artificial leather, industrial catalysis. 39 pictures, 2 figures, and 1 graph. *Popular: raw materials, processes, products, properties. Chemical: research. Selections.*

*372. **Progress of a year—a chemical review.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **18**, 1041–6 (1926).—Research funds, society meetings; illinium, atomic hydrogen, chemotherapy; carbon dioxide ice, ethylene glycol, calcium cyanide, phenol syntheses, rubber accelerators and anti-oxidants, light and electroplated alloys, potash, ammonia, rayon; political and economic chemistry. *Popular: products, properties. Chemical: research. 2 hrs.*

*373. **Synthetic versus natural products.** R. ADAMS. *Ind. Eng. Chem.*, **18**, 1182–6 (1926).—Historical background, dyes, nitrogen fixation, alloys, medicinals, artificial silk, rubber, methyl alcohol. *Popular: historical, raw materials, products, properties. Chemical: research. 1 hr. 40 min.*

374. **Raw materials—waste and by-products.** J. E. TEEPLE. *Ind. Eng. Chem.*, **18**, 1187–90 (1926).—Modes of progress from waste to raw materials occasioned by: legal action against pollution, special demand, sporadic efforts, research, conservation. *Popular: historical, raw materials, products, properties, economics. Chemical: research. 1 hr. 10 min.*

375. **Solid carbon dioxide—a new commercial refrigerant.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **19**, 192–5 (1927).—Previous efforts, manufacturing process, transportation data, 2 pictures. *Popular: products, properties. Engineering: processes, equipment design. 1 hr. 20 min.*

376. **Chromium plating—a new aid to industry.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **19**, 773–6 (1927).—Properties of chromium, conditions of plating, use for decoration and as wear and corrosion resistant. *Popular: processes, products, properties. 1 hr. 10 min.*

377. **Outlets for ammonia—present and prospective.** V. N. MORRIS. *Ind. Eng. Chem.*, **19**, 912–7 (1927).—Oxidation to nitric acid; outlets for nitric acid: ammonium, calcium, and potassium nitrate; outlets for ammonium sulfate, phosphate, chloride, and compounds of ammonia with carbon dioxide. 1 figure. *Chemical: products, properties, research. 1 hr. 50 min.*

*378. **A year's progress in chemistry.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **19**, 1077–82 (1927).—Rubber, petroleum and fuels, ammonia and methanol and hydrocarbon syntheses, carbon dioxide uses, light and chromium alloys, utilization of cellulose waste, reforestation, vitamins, photoelectric cells, prohibition, and political chemistry. *Popular: raw materials, processes, products, properties. Chemical: research. 1 hr. 50 min.*

379. **Chemistry's contribution to automotive transportation.** *Ind. Eng. Chem.*, **19**, 1088–131 (1927).—A series of articles by authorities on metallurgy, nonferrous metals and alloys, aluminum, rubber, automobile glasses, automobile finishes, leather, synthetic resins, textiles, electroplating, fuels, lubricants, anti-freeze compounds, roads, spark-plug insulation, storage battery, abrasives and grindings. 8 pictures. 3 figures. 1 graph. *Popular: processes, products, properties. Chemical: research. Selections.*

380. **Perkin Medal Award to I. Langmuir.** *Ind. Eng. Chem.*, **20**, 329–36 (1928).—W. R. WHITNEY: Langmuir's work; incandescent lamp, atomic welding arc, study of atom, radio tubes. I. LANGMUIR: **Atomic hydrogen as an aid to industrial research.** Gases evolved from lamp filaments, action of hydrogen on tungsten filaments, of nitrogen, gas-filled lamps; need for better education, value of hobbies. 1 portrait. *Chemical: properties, research. 2 hrs. 30 min.*

381. **Chemical control of ventilation at the Holland Tunnel.** S. H. KATZ AND H. W. FREVERT. *Ind. Eng. Chem.*, **20**, 564–70 (1928).—Method of ventilating tunnel. Carbon monoxide: recorders, permissible concentrations, and amounts liberated during the first two days of operation; duties of chemists. 2 pictures, 2 figures, 6 tables. *Engineering: research, equipment design. 1 hr. 30 min.*

382. **Roger Bacon's gunpowder and his secret wisdom.** T. L. DAVIS. *Ind. Eng. Chem.*, **20**, 772–4 (1928).—Quotations from Bacon; the philosopher's egg, black powder. *Popular: products. 50 min.*

*383. **Influence of chemistry on civilization.** J. C. IRVINE. *Ind. Eng. Chem.*, **20**, 884–8 (1928).—The chemist at the breakfast table, tablecloth, morning paper, porridge, spoon and plate, fish, tea, sugar: bread and butter, fuels, morning pipe, final reflections. *Popular: products, economics. 1 hr. 40 min.*

*384. **By-products of chemical warfare.** A. A. FRIES. *Ind. Eng. Chem.*, **20**, 1079–84 (1928).—Protection against marine borers at docks, boll weevils, barnacles; fumigation, ammonia masks, tear gases for controlling mobs, protection against industrial poisoning. 7 pictures. *Popular: properties. Chemical: research. 1 hr. 50 min.*

385. **Chemistry in the food industries.** *Ind. Eng. Chem.*, **20**, 1286–327 (1928).—A series of articles by authorities in the following industries: canning, beverage, baking, chocolate, preserves, citrus products, flavoring extract, shortening, dairy, spice, breakfast food, food regulation, milling, confectionery. 26 pictures. *Popular: processes, products, properties. Chemical: research. Engineering: equipment design. Selections.*

*386. **The Trona enterprise.** C. R. ROBERTSON. *Ind. Eng. Chem.*, **21**, 520–4 (1929).—Isolated Searles Lake, why solar evaporation failed, study of phase diagrams to determine working conditions, plant practice for potash, borax, and boric acid, living conditions, comparison with Stassfurt beds. 3 pictures, 2 graphs. *Chemical: raw materials, processes, products, research. Engineering: equipment design. 1 hr. 40 min.*

387. **Distillation methods, ancient and modern.** G. EGLOFF AND C. D. LOWRY, JR. *Ind. Eng. Chem.*, **21**, 920–3 (1929).—Ancient fractionating towers with several outlets, refluxers, regulation of still head temperature, reboiling of condensate, preheating liquid, and modern application of these principles. Copiously illustrated. 10 pictures, 1 figure. *Popular. Engineering: equipment design. 50 min.*

*388. **Chemistry in incandescent lamp manufacture.** W. J. BARTLETT. *Ind. Eng. Chem.*, **21**, 970–3 (1929).—Tungsten filaments, gases, getters to reduce blackening of the bulb, basing cements, inside frostings, and lamp coatings. 6 pictures, 1 figure. *Popular: processes, properties. Chemical: research. 1 hr. 10 min.*

*389. **Chemistry in the telephone industry.** R. R. WILLIAMS. *Ind. Eng. Chem.*, **22**, 316–22 (1930).—Research in the Bell Telephone Laboratories on dielectric properties, rubber, textiles, paper, plastics, copper, carbon, vacuum-tubes, metals, wood preservation, electrochemical investigations, finishes. 6 pictures. *Popular: raw materials, properties. Chemical: research. 2 hrs. 20 min.*

390. **Chemical industry in the South.** *Ind. Eng. Chem.*, **22**, 412–46 (1930).—A series of articles by industrial leaders: statistical survey of industry and engineering, notable developments, pressure-synthesis operations of the du Pont Ammonia Corporation, carbon dioxide and epsom salt, high-boiling solvents from natural-gas pentanes, enrichment of phosphate rock, wood rosin, celotex and cane-sugar, synthetic-fiber, chemical cotton. 50 pictures, 6 figures, 6 graphs, 5 maps. *Popular: raw materials, properties, products, processes, economics. Engineering: equipment design. Selections.*

391. **Organic fluorides as refrigerants.** T. MIDGLEY AND A. L. HENNE. *Ind. Eng. Chem.*, **22**, 542–5 (1930).—Physical and physiological properties of fluorine and chlorine derivatives of methane; other common refrigerants. 1 picture, 2 graphs. *Chemical: properties, research. 1 hr.*

*392. **Development of the synthetic ammonia industry in the United States.** J. E. CRANE. *Ind. Eng. Chem.*, **22**, 795–9 (1930).—American developments, costs, utilization of ammonia, synthetic alcohols. 3 figures, 3 graphs. *Popular: raw materials, products, economics. 1 hr. 20 min.*

393. **Perkin Medal Award to A. D. Little.** *Ind. Eng. Chem.*, **23**, 235–43 (1931).—F. G. KEYES: accomplishments of the medalist. A. D. LITTLE: **The evaluation of chemical projects.** Financial considerations, growth of chemical industries, development of a project, secret processes, appraisal of project, present industrial situation. 1 portrait. *Popular: raw materials, products, economics, research. 2 hrs. 50 min.*

394. **Solid carbon dioxide from Mexico.** J. W. MARTIN. *Ind. Eng. Chem.*, **23**, 256–8 (1931).—Development of a method for obtaining the natural product; costs. 3 pictures. *Popular: raw materials, processes, products, economics. 1 hr.*

395. **Some recent engineering applications of rubber.** J. R. HOOVER AND F. L. HAUSHALTER. *Ind. Eng. Chem.*, **23**, 462–9 (1931).—Use of rubber in problems of corrosion, abrasion, noise, vibration, insulation, resilience; electrodeposition; removing the aviation ice-hazard. 19 pictures. *Popular: products, properties. Engineering: equipment design. 2 hrs. 20 min.*

396. **Dietary facts and fads.** W. C. ROSE. *Ind. Eng. Chem.*, **23**, 711–7 (1931).—Dietary fads; requirements of an adequate ration including protein, energy, inorganic materials, iodine, vitamins A–G; unsolved problems. *Popular: properties. Biological. 2 hrs. 20 min.*

397. **Manufacture of nitric acid by the oxidation of ammonia.** G. B. TAYLOR, T. H. CHILTON, AND S. L. HANDFORTH. *Ind. Eng. Chem.*, **23**, 860–5 (1931).—Reactions involved, low-pressure plant; experimental, pilot and commercial pressure plants; alternative processes, handling anhydrous ammonia. 12 pictures, 1 figure. *Engineering: advanced, equations, processes, equipment design. 1 hr. 40 min.*

398. **1931 passes in chemical review.** *Ind. Eng. Chem.*, **24**, 5–9 (1932).—Effect of depression upon chemical industry, commercial ventures, pure chemistry and physics. 5 pictures. *Popular: products. Chemical: research. 1 hr. 40 min.*

399. **The handling of corrosive gases.** T. H. CHILTON AND W. R. HUEY. *Ind. Eng. Chem.*, **24**, 125–31 (1932).—Alloys to resist corrosion by moist and hot gases. 11 pictures. *Engineering: equipment design. 1 hr. 40 min.*

400. **X-rays as a research tool in chemistry and industry.** G. L. CLARK. *Ind. Eng. Chem.*, **24**, 182–90 (1932).—Use of X-rays in studies of atomic structure, chemical analysis, iron alloys, grain-size and crystal strain, heat treatment of metals; orientation, shape, and structure of molecules. 11 pictures, 4 figures, 9 graphs. *Chemical: advanced, properties, research. 3 hrs.*

401. **Perkin Medal Award to C. F. Burgess.** *Ind. Eng. Chem.*, **24**, 246–52 (1932).—H. F. WEISS: accomplishments of the medalist. C. F. BURGESS: **Research "for pleasure and for gold."** Research on electrolytic iron, heat; legislation, making research pay; research on cotton, brick; new fields. 1 portrait, 1 picture. *Popular: processes, research. 2 hrs.*

402. **Refrigeration and refrigerants.** D. H. KILLEFFER. *Ind. Eng. Chem.*, **24**, 601–5 (1932).—Application of refrigeration in chemical industries: liquefying gases, solidifying liquids, crystallizing, separating mixtures, regulating reaction velocities, miscellaneous. 3 pictures. *Popular: processes. Engineering: equipment design. 1 hr. 30 min.*

403. **Economic position of sulfur.** A. M. TAYLOR. *Ind. Eng. Chem.*, **24**, 1116–21 (1932).—Sulfur reserves, production of pyrites, recovery of sulfur from gases, consumption of sulfur, sulfur in pulp and paper, sulfuric acid in petroleum industry. 3 pictures, 4 tables. *Popular: raw materials, processes, economics. 1 hr. 40 min.*

404. **Carbon: neglected material of construction for reaction equipment.** C. L. MANTELL. *Ind. Eng. Chem.*, **24**, 1255–9 (1932).—Fabricated forms of amorphous carbon and graphite; resistance to chemical attack and corrosion in acid manufacture, paper making, electrochemical industries and combustion equipment. 8 pictures. *Chemical: products, properties. Chemical: equipment design. 1 hr. 20 min.*

405. **Chemistry in 1932.** *Ind. Eng. Chem.*, **25**, 5–8 (1933).—Vitamins; agriculture, medicinals, physical, and industrial chemical developments; Soviet chemical industry. 2 pictures. *Popular: raw materials, products, properties. Chemical: research. 35 min.*

406. **Sugar industry in foreign lands.** C. A. BROWNE. *Ind. Eng. Chem.*, **25**, 61–8 (1933).—Methods and production of beet sugar in England, France, Germany, Czechoslovakia, Spain; and cane sugar in Arabia and Egypt. 8 pictures. *Popular: raw materials, processes, economics, little chemistry. 1 hr.*

407. **Perkin Medal Award to G. Oenslager.** *Ind. Eng. Chem.*, **25**, 229–37 (1933).—List of achievements of Perkin medalists. H. TRUMBULL: accomplishments of the medalist. G. OENSLAGER: **Organic accelerators.** Early source of crude rubber, improving cheap rubber, organic accelerators including aniline and thiocarbanilide, importance of research in rubber industry. 1 portrait, 3 pictures. *Popular: historical, raw materials, processes, properties. Chemical: research. 1 hr. 30 min.*

*408. **Relation of chemistry to other industry.** C. M. STINE. *Ind. Eng. Chem.*, **25**, 487–95 (1933).—Chemistry 25 years ago and today; progress in dyes, coal-tar, nitrogen fixation, other chemical industries including methanol, hydrogen peroxide, refrigerants, paints, insecticides, cotton; chemical research to offer new products. 4 graphs, 6 charts, 4 pictures. *Popular: products, economics. 1 hr. 15 min.*

*409. **Chandler Lecture: Synthetic organic chemistry in industry.** G. O. CURME. *Ind. Eng. Chem.*, **25**, 582–9 (1933).—Explosives, medicinals, plastics, rayon, dyes, acetylene derivatives, alcohols, rubber, foodstuffs, conclusion. 1 portrait, 2 pictures. *Popular: historical, raw materials, products, properties, organic helps. Chemical: research. 1 hr. 10 min.*

410. **Anode process for rubber articles and coatings.** C. L. BEAL. *Ind. Eng. Chem.*, **25**, 609–13 (1933).—Conditions of concentration, pH, current density, and temperature for electrodeposition of rubber on metals and permeable material; commercial applications, 1 graph, 4 figures. *Chemical: advanced. Engineering: equipment design. 45 min.*

*411. **Applications of vinyl resins.** J. C. DAVIDSON AND H. B. MCCLURE. *Ind. Eng. Chem.*, **25**, 645–52 (1933).—Classification, history, chemical formation, and useful physical properties of vinyl resins; use as lacquers, paneling, furniture, and other household equipment. 5 pictures (4 colored), 2 figures. *Popular: historical, products, properties, little chemistry. 1 hr.*

*412. **Sodium.** H. N. GILBERT, N. D. SCOTT, W. F. ZIMMERLI, AND V. L. HANSLEY. *Ind. Eng. Chem.*, **25**, 735–41 (1933).—Industrial uses in heavy chemicals, dyes, fine chemicals, metallurgy, as a conductor of heat and electricity; physical properties; preparation of sodium ribbon, shot, and colloid; reactions with gases, metals, and organic compounds; use under pressure, in liquid ammonia, as an alloy, as an amalgam; use of sodium amide and sodium alcoholates. 1 picture, 7 figures. *Chemical: raw materials, properties, research. 1 hr. 5 min.*

413. **Laminated safety glass.** G. B. WATKINS. *Ind. Eng. Chem.*, **25**, 1187–91 (1933).—History, principle, and properties of safety glass; types of plastics, laminated plastics, laminating equipment; process of sealing laminated glass, controlling raw material and finished product, comparing strength of plate and safety glass; relation between strength of safety glass and thickness of lamination. 6 pictures. *Popular: historical, products, properties, little chemistry. 50 min.* Also, **Cellulose acetate plastic improves laminated safety glass.** G. B. WATKINS AND J. D. RYAN. *Ibid.*, 1192–5. Comparison between cellulose acetate and cellulose nitrate as a plastic for laminated safety glass as regards resistance to impact, transparency, temperature coefficient, yellowing upon aging, resistance to heat. 3 pictures, 1 graph. *Popular: products, properties. Chemical: research. 35 min.*

414. **Development of new equipment materials for chemical manufacture.** W. R. HUEY. *Ind. Eng. Chem.*, **26**, 10–6 (1934).—Alloys, air-free stoneware, armored silica, beryllium alloys, durichlor, haveg plastics, non-metallic coatings, paints, tantalum, silver, stainless alloys, synthetic rubber, tin plating, transite asbestos cement, future materials. 10 pictures. *Engineering: products, properties, equipment design. 2 hrs.*

415. **Perkin Medal Award to C. G. Fink.** *Ind. Eng. Chem.*, **26**, 232–8 (1934).—H. HIBBERT: Accomplishments of the medalist. C. G. FINK: **Chemistry and art.** Restoration and identification of ancient objects; marbles; electro-osmosis of porous pottery; ivories and wood, insecticides, bronzes, metal plating, air-conditioned museum cases, new fields. 1 portrait, 5 pictures. *Popular: processes, products, properties. 2 hrs. 10 min.*

## SUBJECT INDEX

Starred (*) articles are recommended. Articles in parentheses () furnish incidental information only.

### INORGANIC CHEMISTRY

(Arranged according to the Periodic Table)


**Group 0** **Inert gases,**—*329, 367, (*320, *380, *388). **He,**—367, (333, 364).

**Ia** **H,**— 380, (336, *372). **Alkali metals.** **Na,**—*412, (318, 319, 351). **K,**—328, *339, 357, *386, (319, *372, 377). **$NH_4$,**—(377).

**Ib** **Cu,**—(327, *389, 415). **Ag,**—318, (*371, *383). **Au,**—(340).

**IIa** **Be,**—(*312, 321, 414). **Mg,**—(321, 390). **Alkaline earths,** **Ca,**—301, (370, *371, *373, 377, 415). **Ba,**—(319). **Ra,**—317.

**IIb** **Zn,**—(319). **Cd,**—(316). **Hg,**—(319, 359, *412).

**IIIa** **Rare earths,**—302, Il,—(*372).

**IIIb** **B,**—*339, *386, (321). **Al,**—*303, 340, (*312, 319, *371, 379).

**IVa** **Ti,**—(321). **Zr,**—(314, *321). **Th,**—302, (314).

**IVb** **Si,**—(340, 366, 379, 414). **Glass,**—325, 342, 345, 356, 413, (319, *371, 379, *388). **Quartz,**—(357). **Ceramics,**—327, 379, (369, *371, *383, 401, 415). **Sn,**—(314, 319, 414, 415). **Pb,**—(327, 364, 379).

**Va** **V,**—317. **Ta,**—(357).

**Vb** **N,**—(*380). **$NH_3$,**—311, 336, 377, 397, (314, 333, 357, 364, 366, *372, *373, *378, *384, *392, 408, *412). **$HNO_3$,**—377, 397, (314, 319). **Fertilizers,**—(*306, *307, 340, 356, *371, 404). **Nitrate explosives,**—(333, 340, 366, *371, *409). **P,**—341, (357, 366, 377, 390). **As,**—(334). **Sb,**—(319).

**VIa** **Cr,**—321, 376, (*378, 415). **Mo,**—(321). **W,**—*388, (*320, *369, *380). **U,**— 317, (311).

**VIb** **O,**—329, *306. **S,**—*308, 382, 403, (340, 366). **$H_2SO_4$**—(319, 379, 390, 403, 404). **Se,**—(364).

**VIIb** **Halogens,**—(357, 366). **F,**—325, 391, (*388). **Cl,**—330, 391, (319, 357, 377, 414). **Br,**—(364). **I,**—396, (357). **Oxyacids of the halogens,**—341, (357).

**VIII** **Fe,**—310, 359, (*307, *369). **Co,**—(327). **Ni,**—(316). **Special steels and alloys,**—(316, 319, 333, *338, *371, *372, *373, *378, 379, 400, 401, 414). **Pt,**—*324. **Os,**—(311).


### ORGANIC CHEMISTRY


**Carbon, oxides and carbonates.** C,—*320, *368, 404, (*307, *312, 316, 319, 333, 337, 340, 379, *389). CO,—*368, 381, (336). $CO_2$,—*368, 375, 394, (336, 346, 356, *372, 377, *378, 390). Carbonates,—*368, (415).

**Carbohydrates.** Sugar,—304, 313, 385, 390, 406, (337, *383). Starch,—304.

**Cellulose products,**—Cotton,—(*384, 390, 401, 408). Celluloid,—313 Cellulose esters,—365, 413, (357). Paper,—403, (*371, *383, *389, 404). Rayon,—365, (357, *371, *372, *373, *409).

**Dyes,**—315, 331, 342, (319, 323, 364, *371, *373, 408, *409, *412).

**Drugs, perfumes,**—331, 342, 344, 404, (323, 356, 357, 364, *371, *373, *409).

**Fats, waxes, soaps and oils,**—301, 322, *356, (337, 370, *371, *383).

**Fuels,**—*308, 341, *348, *356, 357, *368, 379, (323, 334, 340, *371, *378, 390, 403).

**General organic.** Acetylene derivatives,—(*409). Acids,—(314, 319, 364). Alcohols,—360, 379, (364, *372, *373, *378, *392, *408, *409, *412). Coal-tar derivatives,—(*371, *372). Distillation,—*371, 387. Flame,—(314). Paints,—(357, 364, *371, 379, 408, 414). Plastics,—318, *411, 413, (389, *409, 414).

**Rubber,**—395, 407, 410, (356, 357, *371, *372, *373, *378, 379, *389, *409, 414).

**Textiles,**—Fabrics,—(*306, *371, *383, *389, 390). Leather,—(*371, 379).


### MISCELLANEOUS


**Biographical,**—*303, *308, 313, 316, 322, 329, *332, 334, *338, *346, 347, 351, *352, 354, *380, 383, 393, 401, 402, 415.

**Branches of chemistry.** Analysis,—*326, *369, (400). Biochemistry,—*346, 350, 360, 362, 370, 396, (337, 338, 347, 356, 357, 372, *378, *384, 405, *409). Catalysis,—311, 336, 390, (304, 322, *371, *372). Colloids,—*352, (329, *335, 337). Electrochemistry,—332, 410, (316, *335, 379, 389, 395, 404, *412). Geology,—(337). Metallurgy,—*371, 412, (*307, 379). Photochemistry,—350, *369, 370, 400, (*306, 316, 333, *335, *348, *371, *378, *380).

**General inorganic.** Alchemy,—353. Art,—415. Atomic structure,—*348, 354, 355, (*335, *369, *380, 400). Corrosion,—359, 399, 404. Dust explosions,—363. Fumigants, and insecticides,—364, *371, *408, (*384, 415). Hydrogen peroxide,—(*408). Refrigeration,—402. Water, —334, 374 (*306, *371).

**Industrial chemistry.** *349, 353, *361, 393. Foreign,—405, 406. Research economics,—305, 309, 310, 313, 315, 318, *320, 331, 358, *361, 374, 393, 398.

**Natural resources.** United States,—386. Other countries,—(323).

**War,**—315, 319, 331, 333, 341, 342, 366, (337, 357, 364, *384).

W. O. Brooks
A. T. Burtsell
R. K. Carleton
Tenney L. Davis
J. Howard Graham
B. Clifford Hendricks
J. W. Howard

# ABSTRACTS

R. A. Baker, *Abstract Editor*

D. C. Lichtenwalner
Greta Oppe

C. M. Pruitt
Leopold Scheflan
A. A. Vernon
E. D. Walter
Mary Elvira Weeks
Sidney Weinhouse
G. H. Woollett

## KEEPING UP WITH CHEMISTRY

**Black magic in the movies.** A. B. Laing. *Chem. & Met. Eng.*, **43**, 424–4 (Aug., 1936).—Chemistry has solved many difficult problems of the moving picture director and offers him an important tool with which to solve countless more. Cobwebs have been made of rubber dusted with fuller's earth. Dry ice controlled by a series of blowers of varying horsepowers is used in present-day "fog sequences." All Hollywood skating rinks were once constructed of plain photographic hypo. By compounding other sodium salts with the hypo, this was made more slippery and longer lasting. A dye has been discovered which will give this hypo ice a bluish tinge. Quiescent volcanoes have erupted at the chemist's behest, spewing powdered aluminum in a thermite mixture. "Cold" fire is another accomplishment. J. W. H.

**How a chemical engineer looks at the farm problem.** A. W. Hixson. *Chem. & Met. Eng.*, **43**, 436–8 (Aug., 1936).—The farmer and the agricultural industry as a whole should fully appreciate the fact that controlling conditions under which they exist are changing rapidly and will continue to do so and that it is necessary to anticipate these changes and make provision for adjusting themselves to them. Many of these changes will be brought about by discoveries in the field of applied chemical science. Research must be undertaken in order to develop non-food uses for standard farm crops in industry. New crops must be developed that will have use as raw materials in industry. Instead of making two blades of grass grow where one grew before, two new uses should be developed for the old crop and two new crops to replace each old useless one. Agriculture should find out how to break up nature's big molecules step by step. This field has tremendous possibilities. The farmer must keep his eye continually on the chemist and chemical engineer. Agricultural experiment stations should reorganize their research programs in the light of the new trends in the scientific and industrial world. They should be staffed with the keenest research minds. If agriculture is again to be prosperous and if industry is to continue its prosperity they must work together and utilize the fruits of their research laboratories for their mutual interest. J. W. H.

**From waste liquor.** Anon. *Ind. Bull. Arthur D. Little, Inc.*, **115**, 2 (Aug., 1936).—This article tells of the industrial significance of yeast as related to the sulfite liquor, a nuisance by-product of the sulfite process for cooking paper pulp. The process was developed by a Swedish engineer and has been in operation in Europe for some time, but only recently in England and in Nova Scotia where waste liquor from newsprint mills is used as the raw material. The waste liquor is treated by aëration, neutralization, and settling to give a product which is ready for inoculation by the yeast organisms. The propagation of the yeast is carried out under conditions similar to those obtaining in molasses yeast cultivation. It is stated that 40 to 55 pounds of yeast per ton of waste liquor is obtained by this method, equivalent to between 350 and 450 pounds per ton of sulfite pulp. Since only the fermentable sugars are utilized in this process, the extraction of lignin and other waste constituents of waste liquors can also be practiced. G. O.

**Chemical agronomy.** Anon. *Ind. Bull. Arthur D. Little, Inc.*, **115**, 3–4 (Aug., 1936).—Chemical agronomy is not so well known, but the possibilities of controlling and modifying plant growth independent of seasons, and of increasing the yield of agricultural products, are already being put into practice as a result of the painstaking research of the chemists and plant physiologists at our many state agricultural experiment stations and private laboratories. Plants are being grown in coarse, clean sand without soil to try to find out the effects of proper fertilizing chemicals added to the water. Vegetables are being grown in tanks of water without any form of soil. Water culture is not new, the idea having been expressed some three hundred years ago. California has carried this idea through now to a commercial basis. Among the advantages of these controlled experiments are the density of the stand of plants that is possible, freedom from soil pests, and longer periods of bearing. Tomatoes are said to yield 217 tons per acre of tank surface per year. Potatoes have yielded at the rate of 2400 bushels per acre. Where the temperature is controlled fruit appears six weeks ahead of that from plants in unheated rooms. There are about thirty elements in plant structures, some being essential while others are thought to be only beneficial. The formulas for chemical nutrients are not being given out until further experimental work can be done, but it is stated that about ten chemical elements are used, all of which are low in cost and mostly products of the heavy chemical industries. The item of labor for such intensive farming is not yet known, but will certainly have a prominent place in any economic comparison between these advanced methods and the older practices. G. O.

**Progress of the beet sugar industry in 1935.** E. O. von Lippmann. *Chem.-Ztg.*, **60**, 127–9 (Feb. 8, 1936).—A survey. L. S.

**The German nitrogen fertilizers, their composition and action.** O. Engels. *Chem.-Ztg.*, **60**, 247–50 (Mar. 21, 1936).—A survey. L. S.

**German zinc.** G. Grothe. *Chem.-Ztg.*, **60** (Mar. 25, 1936).—A survey. L. S.

**The manufacture of sugar, alcohol, and yeast from wood as the raw material.** H. Scholler. *Chem.-Ztg.*, **60**, 293–6 (Apr. 8, 1936).—A survey. L. S.

**Successes and problems of the sugar industry.** E. Gundermann. *Chem.-Ztg.*, **60**, 353–6 (Apr. 29, 1936).—A survey. L. S.

**Danish opium.** H. Baggesgaard-Rasmussen, K. Salomonsen, and J. C. Jespersen. *Chem.-Ztg.*, **60**, 356–7 (Apr. 29, 1936).—A survey. L. S.

**German mercury.** E. Reitler. *Chem.-Ztg.*, **60**, 365–7 (May 2, 1936).—A survey. L. S.

**Tall-oil, a liquid rosin.** C. Becker, Jr. *Chem.-Ztg.*, **60**, 373–5 (May 6, 1936).—The word "tall" comes from the Swedish and means pine. The oil is obtained by treating the resin-containing wood with caustic solutions under pressure for 3–8 hours, thereby dissolving out the resinous constituents. After separation of the alkaline layer the acidic fatty and resinous materials collect on the surface in the form of fatty or resin soaps which are removed and purified. Typical analyses of a good crude and a purified oil are: water 0.5% and 0.05%; ash 0.01% and 0.0%; unsaponifiable 6.97% and 2.95%; resinic acids 30% and 12%; fatty acids 60% and 85%; saponification numbers 180 and 186.5. The freezing point of the purified product is 0.5°C. The oil is used in the manufacture of certain soaps. Its use is limited on account of its pronounced odor. The soap is very soluble and has good foaming and emulsifying properties. L. S.

**Germ-proofing your operation.** J. Stafford. *Sci. News Letter*, **30**, 122–4 (Aug. 22, 1936).—Dr. Deryl Hart of Duke Hospital, Durham, N. C., considers the very atmosphere about a patient upon the operating table to be a menace to the successful healing of the incision. To minimize that hazard he has developed a technic for sterilizing the air by means of ultra-violet light of about 2700 Å. His investigations have shown that when irradiation is used practically all bacteria of the air exposed to the rays were killed, while in corners of the operating room out of the range of the rays 10% to 20% of the bacteria escaped destruction. The procedure is, in some respects, similar to Lister's carbolic acid spray which he tried in his early attempts at antiseptic surgery. B. C. H.

## APPARATUS, DEMONSTRATIONS, AND LABORATORY PRACTICE

**Aluminogel, its preparation and properties.** H. BRÜCKNER AND L. HIRTH. *Angew. Chem.*, **49**, 360–2 (June 6, 1936).—Amorphous active aluminum oxihydrate (aluminogel) is made by the precipitation of aluminum hydroxide from aluminum chloride or sulfate by the addition of ammonium hydroxide, filtering, washing, drying, and compressing. The gel has a hard glassy structure, similar to that of silicic acid, and is not affected by water absorption and regeneration. The total water absorptive power of the completely dehydrated gel is about 40%. The regeneration is carried out by heating the gel in a current of air to 400–500°C. L. S.

**The laboratory preparation of rayon according to the copper process.** R. SCHARF. *Z. phys. chem. Unterricht.*, **49**, 119–20 (May-June, 1936).—Place 3 g. of loosened medical cotton in 90 cc. of Schweitzer's reagent and leave it in a cork-stoppered bottle with occasional shaking for 1–3 days. Then pour the thick dark blue solution into an 8-mm. glass tube about 20–30 cm. long, the lower end of which has been drawn to a fine capillary of a diameter of 0.1–0.5 mm. and bent at a right angle. When the blue solution begins to emerge under its own pressure dip the tube into a precipitation bath consisting of 90 cc. 33% NaOH and 10 cc. anhydrous glycerin contained in a flat glass dish. The slowly emerging blue solution will solidify to an irregular thread of Cu sodium cellulose. To imitate industrial conditions pull the thread slightly with forceps as it is forming. After the thread has been 2–10 minutes in the bath remove it with a glass rod, rinse twice with distilled water for 5 minutes, decolorize in 2% $H_2SO_4$, rinse with water, place in a hot bath containing 1% soap and 1% glycerin in water, and dry without rinsing. Straighten the threads by steaming and stretching. A 0.02-mm. thread will support loads of 20 g. L. S.

**Several lecture experiments on combustion.** K. CLUSIUS AND H. GUTSCHMIDT. *Angew. Chem.*, **49**, 446–7 (July 11, 1936).—The reaction kinetic studies of the last ten years have shown that the oxidation of organic molecules takes place according to a chain mechanism. The essential characteristics of these organic chain reactions are: (1) the oxidation of the compound is retarded by oxygen and hastened by excess of the hydrocarbon; (2) the oxidation is retarded by antiknock agents, like iron penta carbonyl, selenium tetraethyl, as the chains are disrupted by the oxidation products of these agents; (3) the oxidation is hastened by catalysts or promoters which start new chains. The following apparatus was used. A 1-liter cylindrical sheet-iron vessel (3-mm. wall, 9-cm. diameter, 16 cm. high) was covered on the outside with asbestos and resistance wire. A bottom and top were welded to the cylinder and a hole (2 cm. in diameter) was made in the center of the top. A short 8–10-mm. thin-walled steel air-inlet tube was inserted near the bottom and extended by means of a German silver tube (German silver has low heat conductivity). The whole was insulated thermally by covering with kieselguhr or magnesia in a large sheet-metal box. A protected thermoelement was placed in the oven and connected to a calibrated temperature-measuring device, which was directly visible to the audience. About 20 cm. above the oven was placed a small buret from which the organic liquid could be dropped into the oven. An asbestos and copper sheet shielded the buret from heat as much as possible. Directions are given for conducting suitable experiments, and curves show the lowering of the ignition temperature of benzine by aldehyde and the lowering of the ignition temperature of benzine, hexane, and benzol by ethyl nitrite and the addition of $NO_2$ to the air. L. S.

**The absorption of light and its importance in chemistry.** See this title under Scientific Reviews and Bibliographies; Tabulations of Scientific Data.

## SCIENTIFIC REVIEWS AND BIBLIOGRAPHIES; TABULATIONS OF SCIENTIFIC DATA

**The absorption of light and its importance in chemistry.** H. FROMHERZ. *Chem.-Ztg.*, **60**, 445–8 (May 30, 1936).—Nearly always solutions of light-absorbing compounds are used in chemical studies of light absorption. Those compounds are employed for solvents which in the visible or neighboring ultra-violet region (down to 180$\mu$) do not absorb, as, *e. g.*, water, alcohol, hexane, etc. The absorption in such solutions follows Beer-Lambert's law:

$$\frac{I}{I_0} = 10^{-kcd} \qquad k = \frac{1}{cd} \log \frac{I_0}{I}$$

where $d$ = thickness of plane parallel, vertically irradiated layer of solution in cm., $I_0$ = intensity of incident ray, $I$ = intensity of emerging ray, $c$ = concentration in moles per liter, and $k$ = molar extinction coefficient. The spectral position, height, and width of the absorption band of a compound are characteristic for this compound or a chemical group of this compound. Chemically similar compounds have similar absorption curves. If the absorbing ions or groups in a compound have no influence on one another then the absorption curve of the compound is an addition product of the absorption curves of the separate groups. No such additivity exists if the absorbing groups in a compound act upon each other chemically or are altered by an external action. A change in the solvent produces a shift in the spectral position of the absorption band by several $\mu$ if no chemical action occurs. The highest absorption maximum of an inorganic or organic compound lies usually between $\log k = 3.5$ and 4.5. If the $\log k < 1$ for a particular absorption maximum it is due to impurities or rearrangements. The foregoing facts are illustrated with various examples, and applications are described for determining the concentration and constitution of a number of materials. L. S.

**Science reading materials for pupils and teachers.** C. M. PRUITT. *Sci. Educ.*, **20**, 83–99 (Apr., 1936).—This is a practically complete bibliography of science books for pupils and teachers covering the period 1932–1935. The teacher references include a list of professional books for teachers. Books are listed according to subject. C. M. P.

**Artificial radioactivity.** M. DIERSCHE. *Chem.-Ztg.*, **60**, 87–8 (Jan. 25, 1936).—A survey. L. S.

**Chemical uses of alkali salts.** B. WAESER. *Chem.-Ztg.*, **60**, 93–6 (Jan. 29, 1936).—A survey. L. S.

**Heavy hydrogen. Its importance in the study of chemical and biological problems.** W. BRANDT. *Chem.-Ztg.*, **60**, 285–8 (Apr. 4, 1936).—A survey. L. S.

## ADMINISTRATIVE PROBLEMS AND DEVICES; CURRICULA

**An integration of physics and chemistry.** H. E. WISE. *Sci. Educ.*, **20**, 68–72 (Apr., 1936).—This article presents the results of an attempt to integrate certain selected portions of the traditional physics and chemistry courses in the senior high school of Teachers College of the University of Nebraska. The following problems were selected. (1) What is matter, and how is it affected by chemical and physical forces? (2) How do fluids respond when chemical and physical forces are made to act upon them? (3) How do scientists represent chemical and physical changes? (4) What is heat, and how does heat contribute to physical and chemical changes? (5) What are acids, bases, and salts, and how do they behave in solution? (6) What is the nature of metals, and how are metals used in doing work? (7) How may electricity be produced, and what are the physical and chemical effects of the electric current? (8) What is the physical and chemical nature of non-metals? (9) What is the nature of light, and how is light affected by the media which it encounters? (10) What is the nature of sound, and what are the effects of sound energy? C. M. P.

**Integrated education in the Lincoln School.** SYMPOSIUM. *Teachers Coll. Rec.*, **37**, 363–447 (Feb., 1936).—The following phases of the integrated educational program of Lincoln School of Teachers College are discussed. (1) Integration in the Lincoln School Philosophy, by Lester Dix; (2) Life in the Elementary School, by Rebecca J. Coffin; (3) The Arts in the New Curriculum, by Alice Schoelkopf; (4) Leisure in the New Curriculum, by Ouida Meyer; (5) Life in the High School, by John R. Clark; (6) Integration in the Junior High School, by Frances G. Sweeney; (7) Integration in the Senior High School, by L. Thomas Hopkins; (8) World Literature, by B. J. R. Stolper; (9) American Culture, by Edwin S. Fulcomer; (10) Foreign Languages at Lincoln School, by Frederick J. Rex and Jane E. Brown; (11) Guidance in the Lincoln School, by Gertrude H. Hildreth; (12) Curriculum Development, by L. Thomas Hopkins; and (13) Science in the Junior High School, by H. Emmett Brown, Hubert M. Evans, and N. Eldred Bingham. C. M. P.

## THE PHILOSOPHY OF EDUCATION

**Knowledge versus thinking.** B. D. WOOD AND F. S. BEERS. *Teachers Coll. Rec.*, **37**, 487–99 (Mar., 1936).—The authors contend that thinking depends upon knowledge and facts—without these two there can be no thinking. They answer the question "Can Teachers Create Thinkers?" negatively. "Those who prefer thinking unfettered by facts display a deep fear of rote memory and a militant suspicion of anything which even superficially suggests that remembering is not a criminal act..... The generalization that 'the purpose of the social sciences is to teach students to apply the principles and generalizations of the social sciences to new social problems' or 'to train students to deal with the problems of a changing civilization' seems to be an excellent example of an empty generalization—a verbal fetish whose futility thrives as the inevitable result of the cult of thinking that is largely and almost arrogantly unfettered by mere facts.... So far as a deeply sympathetic observer can see, social science teachers as a group are not notably distinguishable from other teaching groups in regard to citizenship. They are not ordinarily regarded as better citizens, or more unselfish in economic or social conduct, or as more intelligent voters, or as affording more and better leadership in social emergencies than other teaching groups." C. M. P.

**Teaching science for the purpose of influencing behavior.** V. H. NOLL. *Sci. Educ.*, **20**, 17–20 (Feb., 1936).—The author discusses some of the principles that are of primary importance in the teaching of science for purposes of influencing behavior. (1) Desired attitudes which are to influence behavior must be taught directly; (2) if we wish to develop the scientific attitude, our pupils must be given the opportunity to practice such an attitude; (3) if the scientific attitude or other attitudes are to function in everyday life, there must be specific provision made in our teaching for generalizing these attitudes; and (4) if the scientific attitude or habits of scientific thinking are to become a part of the nervous systems of boys and girls in our schools, they must be made objectives desirable to them. C. M. P.

**Science in education.** K. T. COMPTON. *Sci. Educ.*, **20**, 53–5 (Apr., 1936).—This brief paper deals with two aspects of the subject: (1) the place of science in education, and (2) some problems of education in science. In early days science was secret; its devotees were a secret cult; it was like an aristocracy—not for the common people. Today science is an integral part of the daily interest and life of everyone—science has become a democracy. Superstition is a matter of the emotions; science is a matter of reason. Both a thorough knowledge of the subject to be taught and expert training or native skill in the abstract art of teaching are necessary for a good teacher.

C. M. P.

## GENERAL

**Patent anniversary.** ANON. *Ind. Bull. Arthur D. Little, Inc.*, **113**, 2–3 (June, 1936).—July, 1936, marked the centennial of the present patent system of the U. S. The U. S. patent system is recognized as being an important factor in the industrial and technical life of this country. While the same thing is true of other countries, there is a significant difference that should be borne in mind before we adopt any procedures used abroad. The American Constitution, wherein the basis of patent protection was established, *secured* the *rights* of inventors to their inventions; while in Great Britain the purpose is to *grant* a *privilege* to inventors. The U. S. recognizes the inherent right of the inventor to his inventive property; the latter is in the nature of a grant by the Crown of monopolistic concession. Patents abroad are generally regarded as a convenient source of tax income, while our country stands almost alone in requiring no taxation of issued patents. Although the foundation of the patent system was laid in 1836, it has been revised many times since, indicating a healthy state of progress—contrary to the ideas of many who think the patent system entirely static.

G. O.

**Dangers of regimentation and complacency.** K. T. COMPTON. *Chem. & Met. Eng.*, **43**, 355–8 (July, 1936).—Two conditions which threaten the progressive work of science are the philosophy of regimentation and complacency. Some are advocating a policy whereby the developments in the natural sciences should be brought under the control and supervision of the social scientists in order that our civilization might progress along the lines of a campaign planned by them. One of the worst features of this attitude is the reliance on rules and regulations, even in matters whose success or failure is absolutely dependent on scientific knowledge and skill.

The lumber industry and the railroads are cited as examples of industries which have suffered because of their complacent attitude. Every organization should adopt the fundamental policy of carrying on in such manner as to give the best possible service to the public. J. W. H.

**Specially designed equipment.** W. SPOONER. *Chem. Industries*, **38**, 586–8 (1936).—"When individualism was really rugged, standardization was the idealist's dream. Each separate plant was run according to the ideas of its management and ideas as to equipment were as individualistic as the choice in neckties. Even boilers were likely to be of specific design. Electric power and the tremendous technological advances of the past half century led a long swing in the opposite direction, which is not without its bad aspects.

"The X Y Z Soap Company, making household and toilet soaps, may well use crutchers, frames, glycerin stills, etc., of standard design, exactly similar to the equipment at the A B C Soap Company, because processes and products are virtually the same. Every justification exists for such standardization, for an industry inevitably develops equipment embodying past experience and leading to the best production economy and efficiency.

"Suppose, however, one of these imaginary companies produces a new sulfonated oil shampoo, involving rather delicate blending and heating operations at one stage of production. It could take a standard type of jacketed mixer and adapt its design and operating characteristics to the special production problems involved in the new shampoo. In the end, a shampoo would be successfully produced but either the process or product would have had to be modified, in which case the possibility of developing a really outstanding new shampoo might be put in real jeopardy, or the equipment would be so modified and adapted as to become, for all practical purposes, a specially designed unit."

A. T. B.

**Biology as a science helpful to the field of chemistry.** W. SCHWARTZ. *Chem.-Ztg.*, **60**, 105–7 (Feb. 1, 1936).—The relationships reviewed connecting biology and chemistry deal with textile chemistry, agricultural chemistry, the artificial fertilizer industry, protection of plants, drugs, and the fermentation industry. L. S.

**A novel experiment.** S. B. ARENSON. *Sch. & Soc.*, **44** (July 4, 1936).—"Last year, the University of Cincinnati inaugurated a series of lectures, 'The Applications of the Physical Sciences,' to honor those high-school junior and senior students ranking highest in their classes in chemistry, physics, or advanced mathematics. On ten successive Saturday mornings, 400 to 600 of the 660 invited students, recommended by their teachers as being among the top 10 per cent. of their science classes in metropolitan Cincinnati, gathered at the largest auditorium on the campus for these lecture demonstrations. Admission was free, but by invitation only, each student being supplied with a ticket for the entire series. Each talk was illustrated by demonstrations, slides, or motion pictures."

"It was deemed advisable to refuse the petitions of scores of teachers, who, naturally being interested, asked that they be permitted to attend these lectures along with their students. However, this year, a new series of lectures was devised, which was given first to the teachers alone, and later to the pupils."

"The second series for the students has just been completed. These new lectures were received with more enthusiasm, if possible, than the original series."

"It is the plan to alternate these two series. In this way the eligible junior and senior high-school students will get an opportunity to hear both series during their last two years in high school."

The lecture titles and lecturers of the series to date are listed.

O. R.

# RECENT BOOKS

INORGANIC CHEMISTRY FOR COLLEGES. *William Foster*, Ph.D., Russell Wellman Moore Professor of Chemistry, Princeton University. Second edition. D. Van Nostrand Co., New York City, 1936. x + 925 pp. 216 figs. 13.5 × 21.5 cm. $3.90.

This new edition follows the general plan of the previous one, but many portions have been rewritten so as to include new developments in the science.

An entire chapter has been devoted to atomic structure, including a modified Bohr-Thomsen periodic table, the electron theory of valence, heavy hydrogen and heavy water, transmutation of the elements, and a brief statement of the quantum theory. The chapters on ionization have been modernized, and the new definitions of acid and base are given. New problems have been introduced, and the reading references at the ends of the chapters have been extended.

Like the first edition, this book will appeal particularly to the student in chemistry who is interested in a reference book which covers the whole science in an introductory way.

J. H. REEDY

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AN INTRODUCTION TO ORGANIC CHEMISTRY. *Alexander Lowy*, Ph.D., Professor of Organic Chemistry, University of Pittsburgh, and *Benjamin Harrow*, Ph.D., Associate Professor of Chemistry, College of the City of New York. Fourth edition. John Wiley & Sons, Inc., New York City, 1936. xiv + 429 pp. 15 × 23 cm. $3.00.

The authors and publishers of this text, apparently in their desire to keep the contents abreast of current developments in the field of organic chemistry, have consistently revised this volume every four years since its first appearance in 1924. This new fourth edition includes "besides considerable additional material, the more important recent advances in the field of organic chemistry, at least, such of them as are suitable for an elementary text," according to the authors. "The nomenclature has been revised, wherever necessary," to conform to present usage. A new chart, summarizing many of the important reactions of acetylene and products derived from it, has been added. The reading references at the end of each chapter and the additional reference books at the end have been brought up to date.

The authors have attempted to embody in this text the well-recognized basic principles of organic chemistry, its recent developments and important applications. Illustrative material has been selected extensively from the fields of medicine, dentistry, pharmacy, agriculture, and other biological sciences. As a result, chapters dealing with lipoids, nucleoproteins, foodstuffs and their changes in the body, plant and animal pigments, enzymes, vitamins, hormones, and similar topics have been included. The authors consider it suitable for use in connection with a lecture course meeting two hours a week over a period of two semesters.

The major criticism of this text, in the opinion of the reviewer, is that the treatment of subject matter may be too brief and inadequate at times, particularly for the student with the chemistry major. The topics are well-organized clear, and logical, but almost assume outline form at times where a more extensive discussion would be better. However, this difficulty can be largely overcome by the student who will read extensively from the numerous references at the end of each chapter, or by the well-informed instructor who can read between the lines and will supplement the brief treatment in the text with additional material and detail during the lecture period. While many new topics have been added or expanded, such as the tetrahedral carbon atom, phenol from chlorobenzene, etc., many instructors will still wish that the treatment might have been more extensive. Other topics such as kelation, rotenone, etc., have been entirely omitted, but these, perhaps, are beyond the scope of this volume and belong essentially in advanced or graduate courses. Practically all equations are written structurally, greatly simplifying their interpretation by the student. A large amount of useful information is neatly arranged in table and outline form.

This volume contains many commendable features to recommend it to both students and instructors. The style is unusually clear and logical. Relationships between the various organic types are more clearly shown than in most similar volumes. The last chapter deals with nomenclature (American practice) and is so located that it is readily available for reference use. Numerous tables and charts (some in two colors) add a large amount of supplementary information. Reading references are extensive, up to date, and of a type that should be readily available in most college and university libraries. Sufficient material on recent organic advances has been added to this fourth edition to make a distinct improvement over the previous edition. Biological topics, such as vitamins, enzymes and hormones, proteins and foodstuffs in the body, etc., have been extended. Many instructors will welcome the inclusion of several portraits of prominent organic chemists, including four living Americans.

The book is neatly and substantially bound. It is remarkably free from typographical errors. Reading is easy, and is improved by the pleasing arrangement and extensive use of structural formulas and charts. The volume should be a valuable reference book on any organic chemist's desk, and should continue to be a leader among texts for two-semester courses in introductory organic chemistry.

RALPH E. DUNBAR

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PHYSICAL CHEMISTRY FOR COLLEGES. A Course of Instruction Based upon the Fundamental Laws of Chemistry. *E. B. Millard*, Professor of Physical Chemistry, Massachusetts Institute of Technology. Fourth edition. McGraw-Hill Book Co., Inc., New York City, 1936. ix + 524 pp. 14 × 20.4 cm. $3.75.

This excellent textbook, now in its fourth edition, first appeared in 1921. The author states in the preface: "The acquisition of a chemical education may be represented figuratively by progress along a spiral path about a perpendicular erected at the common intersection of these fields [inorganic, organic, analytical, and physecal], and the utmost capacity of an undergraduate student will not represent more than two revolutions of such a spiral. Thus he passes over each field twice, and it would be an extravagance to claim, or to allow him to believe, that he has mastered a broad field by so doing. . . . The author has endeavored to adjust the pitch of the spiral so that the student will be stimulated without being discouraged." In this aim the author has succeeded in an unusual degree, and the widely diverse subdivisions of the subject have been correlated so as to give the student a unified working knowledge.

The present edition presents a considerable number of improvements in the subject matter. The chapter on "Physical Properties and Molecular Structure" has been entirely deleted, and a chapter on "Free Energy and Chemical Change" added. The laws of thermodynamics have been elaborated and stated, though briefly, in mathematical terms. The chapter on "Solid Substances" has been extensively revised, giving a more detailed discussion of powder photograms, unit cells of various space lattices, and the crystal structure of compounds.

Particularly noticeable throughout the book is the attitude of conservatism adopted by the author. For example, on page 75 of the third edition the statement is made: "The cause of molecular attraction is *not fully* understood." In the present edition, on page 81, the author is not willing to concede even a partial knowledge of the phenomenon, stating that "the cause

of molecular attraction is *not at all* understood." Another desirable improvement is the omission of many of the purely empirical equations, such as Prud'homme's equation connecting absolute boiling point, melting point, and critical temperature of liquids; Arrhenius' equation representing the viscosity of a liquid as a function of the temperature; and the empirical ionization equations for strong electrolytes. An empirical equation, based as it is upon limited data, is often little more than a lucky guess, and may have no relation to the mechanism of the process. It usually contains a number of constants which must be determined for each substance or reaction, and is thus limited in its applicability. The reviewer is mindful of the fact that a purely empirical equation is better than none at all for calculating unknown quantities and that even our most important equations contain specific constants. However, in the teaching of physical chemistry, the emphasis needs to be placed upon those well-established principles and equations which have been repeatedly verified and whose correctness is generally recognized.

From the mechanical standpoint the book represents an improvement over previous editions. The book manifests the same superior quality of workmanship which has consistently characterized the International Chemical Series. Readers will welcome the elimination of troublesome diagonals in the printing of mathematical formulas. Cuts have been reduced in size, and derivations of formulas, formerly in footnotes, moved up into the body of the text. The book is strikingly free from typographical errors, only one coming to the reviewer's attention, namely, Poiseuille, which on page 100 is rendered "Poiseville." A certain inconsistency in the use of chemical terms is apparent in numerous places. For example, on pp. 84 and 157, both "benzene" and "benzol" are used. On page 162, the author uses the accepted term "diphenyl" but on pp. 350–1, "biphenyl" and "bibenzyl." Although chemical terminology is largely arbitrary, it is desirable that it be consistent and uniform throughout the book.

One must recognize that the revision of such a book, involving as it does the elimination of less important material, a critical selection, digestion and assembly of new knowledge, and the correction of previous errors, is at best a prodigious task. In the present instance, the author deserves commendation for the success he has achieved. As a means of imparting a thorough fundamental knowledge of the subject, the book deserves wide adoption as a text in the first course in physical chemistry.

T. F. BUEHRER

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THE THERMOCHEMISTRY OF THE CHEMICAL SUBSTANCES. *F. Russell Bichowsky*, Editor for Thermochemistry for the *International Critical Tables*, and *Frederick D. Rossini*, Scientist in Physical Chemistry at the National Bureau of Standards. Reinhold Publishing Corporation, New York City, 1936. 460 pp. 15 × 23 cm. $7.00.

The scope and plan of organization of this useful compilation are best indicated by quotations from the preface.

"There are four main sections to the present book: (1), the introduction or explanatory part; (2), the table of heats of formation, which is the fruit of the work; (3), the text, in which the original published data are cited and discussed; and (4), the list of references to the literature, which includes references to all the published data bearing on thermochemistry."

"The table of values contains a list of all the chemical substances (except carbon compounds containing more than 2 carbon atoms), for which there are thermochemical data, together with values for the heats of formation (or heat of transition, fusion, or vaporization) of each substance. It was deemed expedient not to include in the present table values for the heats of formation of carbon compounds containing more than two carbon atoms. It should be possible to obtain from this table, by simple addition and subtraction, the heat of any process involving any of the substances given, with an accuracy as great as is actually known. There are listed in the table 5840 values of heats of formation, and, in addition, 350 values of heats of transition, fusion, vaporization, or reaction, for substances for which no values are given for the heat of formation."

"In the list of references are given the citations to the literature for all the published works bearing on thermochemistry which are discussed or mentioned in the text. This list of 3730 references includes all the publications covered by *Chemical Abstracts* up to January 1, 1931, and nearly all of the important and significant contributions which have been published in the period from January 1, 1931, to January 1, 1934."

"The standard temperature selected for the values given in this book is 18° Centigrade, following the procedure of the thermochemistry section (Bichowsky) of the *International Critical Tables*. The authors have been reluctant not to use the almost universally accepted standard temperature of 25° Centigrade for thermodynamic calculations; but the selection of 18° as the standard temperature is practically necessary in this case because all of the monumental work of Julius Thomsen and of Marcellin Berthelot was done at or near 18° and there are not now available sufficient heat capacity data with which to make accurate conversion to 25° (this is especially important for reactions involving substances in aqueous solution where the temperature coefficient is usually very large). In later years, as the data on heat capacities become available, or as the heats of many of the reactions, which have until the present time been measured only by Thomsen or Berthelot or both, are redetermined, it will be quite feasible to use 25° as the standard temperature."

One may perhaps hope that in a future edition the compilers and publishers will see fit to include 25° values, even though it be impossible to convert the entire compilation to this self-consistent basis.

OTTO REINMUTH

SEMI-MICRO QUALITATIVE ANALYSIS. *Carl J. Engelder*, Professor of Analytical Chemistry, University of Pittsburgh, *Tobias H. Dunkelberger*, University of Pittsburgh, and *William J. Schiller*, Mount Mercy College, Pittsburgh. John Wiley & Sons, Inc., New York City, 1936. x + 265 pp. 14.5 × 23 cm. $2.75.

The text "Semi-Micro Qualitative Analysis" represents an innovation in the teaching of the subject of qualitative analysis to beginning students. It introduces new ideas which, without doubt, are a great improvement over the usual macro methods and procedures. It is a great pleasure to learn that these semi-micro methods have now been made available to students engaged in a study of the subject of qualitative analysis for the first time. The project is to be highly recommended; it is a desirable as well as a distinctive contribution to the teaching of chemistry.

The advantages of dealing with drops or at the most 1–2 cc. of solution are quite evident. Considerable time is saved the student in carrying out filtrations, washings, evaporations, and handling of apparatus and solutions. Precipitation of the sulfides by hydrogen sulfide is facilitated and, in addition, since relatively small amounts of the gas are required for the procedures, it does not become a serious problem in the contamination of the atmosphere of the laboratory. Dealing with small quantities of materials imparts to the student the necessity of exercising care in his manipulations and, above all, naturally leads to neatness. Another major advantage is the saving made in the expense required to provide for laboratory work. Large amounts of chemicals and large pieces of apparatus are no longer indispensable.

The procedures described by the authors are not intended to be of the "micro" type. They appear to have reached the conclusion through experience that procedures intermediate between the usual "macro" and the real "micro" schemes are the most suitable for the beginning student. In this way the principles of ionic equilibria and the chemistry of the more common positive and negative ions are preserved. Group precipitations and separations are carried out in accordance with the usual macro schemes, with the exception that the amount of solution or material to be analyzed is reduced to a practicable minimum.

In addition, methods for identifying the ions, provided they are adequate, are of the same nature as those employed in the macro methods. Wherever these methods are found to be inadequate, more sensitive tests involving organic reagents are used instead. The confirmatory tests make use of such reagents almost exclusively.

The technic of working with a drop or a few drops of solution has been highly developed by Feigl and co-workers; it is known as the "drop-reaction" technic. The microscope is not required here. However, a small hand centrifuge is used to carry out precipitations, while the supernatant liquid is removed with a capillary pipet. Spot plates, both white and black, are also used for precipitation processes. Small funnels, suction flasks and test-tubes, and ordinary medicine droppers make up an important part of the equipment. Organic reagents are used for the more sensitive tests but none of these is absolutely specific; group separations and the elimination of interfering ions must first be accomplished.

The text is divided into four parts: (1) Fundamental Principles of Qualitative Analysis, (2) The Reactions of the Cations, (3) The Reactions of the Anions, and (4) Systematic Microanalysis. The first part contains the usual treatment of the law of chemical equilibrium, ionization, solubility-product principle, hydrolysis, amphoteric substances, complex ions, oxidation and reduction, and the structure of molecules. It comprises about 100 pages of the text. It is unfortunate that strong electrolytes are treated as being partially ionized and thereby capable of contributing to the displacement of ionic equilibria.

Part 2 includes a discussion of the chemical properties of the positive ions, various tests for each ion, including inorganic as well as organic reagents, methods for carrying out the tests, and procedures for practice analysis of the different groups. The semimicro technic is stressed throughout this section. It is gratifying to see that there are made available to the student several tests for each ion. This section also includes numerous references to the literature concerning spot-reaction tests, the use of organic reagents, and the elimination of interfering ions.

The following anions are included in Part 3: nitrite, cyanide, sulfide, thiosulfate, sulfite, carbonate, arsenite, arsenate, phosphate, silicate, fluoride, chromate, sulfate, borate, oxalate, tartrate, ferricyanide, ferrocyanide, thiocyanate, iodide, bromide, chloride, nitrate, and acetate. The semimicro technic is likewise stressed in this section.

Part 4 describes methods of procedure for the preliminary examination of the unknown, systematic cation analysis, systematic anion analysis, and the analysis of insoluble substances.

The Appendix gives the following tables: atomic weights, solubility of inorganic salts, periodic system of the elements, composition of test solutions, lists of apparatus, and methods for the preparation of liquid reagents of all types.

The text is remarkably free from errors and appears in well-printed form.

The authors are to be congratulated on the initiation of a text of this type. Without doubt the teacher of qualitative analysis will receive from it a fresh point of view and renewed inspiration in the presentation of the laboratory work. Certainly, the student will show a greater interest and thereby benefit considerably in the application of the semimicro technic to his laboratory problems.

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COLLOID SYMPOSIUM MONOGRAPH. Papers Presented at the Twelfth Symposium on Colloid Chemistry, Ithaca, New York, June, 1935. Edited by *Harry Boyer Weiser*. The Williams & Wilkins Company, Baltimore, 1936. 156 pp. 17 × 25 cm. $3.00.

The contents are as follows:

The Constitution of Hydrous Oxide Sols from X-ray Diffraction Studies. Harry B. Weiser and W. O. Milligan.

Electrokinetics. XVI. Streaming Potential in Small Capillaries. Henry B. Bull and Laurence S. Moyer.

Studies on Silicic Acid Gels. VI. Influence of Temperature and Acid upon the Time of Set. Charles B. Hurd.

X-ray Spectrography of Alkali Celluloses. John B. Calkin.

The Oxide Film on Passive Iron. Wilder D. Bancroft and J. D. Porter.

The Phase Rule in Colloid Chemistry. Wilder D. Bancroft.

The Determination of Contact Angles from Measurements of the Dimensions of Small Bubbles and Drops. II. The Sessile Drop Method for Obtuse Angles. Guilford L. Mack and Dorothy A. Lee.

Adsorption at Crystal-Solution Interfaces. IX. The Concentration of Foreign Substances in Solution Relative to the Quantity Adsorbed by the Host Crystal. Wesley G. France and Phoebe P. Davis.

Spectroscopic Estimation of Adsorbed Ions. May Annetts and Lorne Newman.

Vapor Pressure—Water Content Relations for Certain Typical Soil Colloids. Lyle T. Alexander and M. M. Haring.

Stream Potentials and D. C. Surface Conductivities in Small Capillaries. H. L. White, Betty Monaghan, and Frank Urban.

Adsorption by Diatomaceous Filters. Earl J. Hoagland and John E. Rutzler, Jr.

Adsorption and Diffusion in Zeolite Crystals. Arne Tiselius.

Dynamic Dispersions and Emulsification. C. H. M. Roberts.

The Adsorption of Water Vapor by the Growth Elements of the Sapwood and by the Heartwood of Southern Pine. C. J. Frosch.

A Hydrate Decomposition Mechanism. V. R. Damerell and O. F. Tower.

OTTO REINMUTH

PROSPERITY BECKONS. DAWN OF THE ALCOHOL ERA. *William J. Hale.* The Stratford Company, Boston, 1936. ii + 201 pp. 13 × 19 cm. $2.00.

The passing of the petroleum era and the beginning of the alcohol era is the main thesis of this interesting and thought-provoking book by Dr. William J. Hale. Under a scientifically controlled social and economic system, which the author calls "chemeconomics," the end of unemployment is visualized with the transfer of millions of workers to the farm. Dr. Hale regards the modern chemical revolution as of even greater significance than the industrial revolution of a century ago. He condemns roundly the modern devices of limiting production to raise prices as false recovery under a "famine-dole" system.

The production of food and raiment, now the major concern of agriculture, the author thinks will be of lesser magnitude in the future than the growing of raw materials for industry. Alcohol is to be the largest single product of agriculture. Dr. Hale regards alcohol as an ideal motor fuel, to be gradually substituted for gasoline. It is also to be the starting substance for many synthetic products. The carbon dioxide evolved in fermentation is to be applied to plants growing in fertilized damp soil under transparent sheets of cellulose acetate or similar material also derived from agriculture, both for increasing yields and rendering the farmer independent of climatic extremes.

Dr. Hale believes that under the chemeconomic system foreign trade in organic materials would become comparatively insignificant. He advocates national self-sufficiency, arguing that it is expensive to transport farm products which are mainly carbon dioxide and water. He believes strongly in profit as an incentive to industry and progress, but urges larger participation of labor in corporate ownership.

The book is written in a popular and entertaining style. The treatment is not detached and objective, the author being a frank and vigorous advocate of chemurgy, chemeconomics, and the alcohol era. Chemists will find this book inspiring in the vision it brings of greater opportunity, and business men will find it valuable for the idea of a new economic system based on the chemical transformation of farm products into the articles of industry.

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